

**REMARKS**Regarding the Amendments to the Specification

The amendments made to the specification by this current response do not add new matter to the specification. In particular, applicants note that the added and amended paragraphs are derived from U.S. Serial No. 09/088,300 (now issued U.S. Patent No. 6,068,861). See U.S. Patent No. 6,068,861, column 2, line 64 – column 3, line 11; column 3, lines 41-53; column 4, line 20; column 5, lines 1-16; column 5, line 58 – column 6, line 6, and column 6, lines 7-23. U.S. Serial No. 09/088,300, from which the current application claims priority as a continuation-in-part, was incorporated by reference in its entirety by the current application as originally filed. See page 1, lines 2-4, and page 14, lines 5-6 of the current application.

Regarding the Amendments to the Claims

Claims 61-65 are currently pending in the present application. By the current amendment, these claims are cancelled in favor of newly added claims 71-130. Applicants note that at the time of filing the current application, claim fees for 60 claims (including for 6 independent claims) was paid. Since by the current amendment, only sixty claims will be pending (6 of them independent), no additional claim fees are believed due.

Claims 71-130 do not add new matter to the specification, and are fully supported in view of the current amendments to the specification which as noted previously, are fully supported in the application as filed in view of the incorporation of U.S. Serial No. 09/088,300 in its entirety. The purpose of the amendments is to pursue a scope of the invention which is not specifically claimed in any of the patents and applications related to U.S. Serial No. 09/088,300. For purposes of full disclosure, Applicants note that the patents and applications related to U.S. Serial No. 09/088,300 (now U.S. Patent No. 6,068,861) include: U.S. Patent Nos. 6,299,909, 6,306,441, 6,322,822, 6,348,219, 6,352,725, 6,495,169, 6,506,418, 6,511,682, 6,652,889, 7,087,251 and 7,195,782; and U.S. Serial Nos. 09/785,890, 10/282,290 and 10/703,311. In particular, Applicants note that the newly added claims are directed to methods of using of the aqueous biocidal solutions which are the subject of claims currently pending in U.S. Serial No. 09/785,890. See Applicants' Response submitted 12/8/08 to the 8/8/08 Office Action in the prosecution file of U.S. Serial No. 09/785,890.

Regarding Patentability Over the Prior Art

Applicants' Response submitted 12/8/08 to the 8/8/08 Office Action in U.S. Serial No. 09/785,890 (hereafter, "the '890 application") extensively discusses the patentability over the prior art (including the Goodenough patent – U.S. Patent No. 3,558,503) of the aqueous biocidal solutions which are recited in the now pending claims of the '890 application, and which are likewise called for in the method of use claims newly added by the present amendment in the current application. Applicants' response submitted in the '890 application was accompanied by extensive documentary evidence, including an affidavit and numerous art publications. Applicants submit that the method of use claims which are the subject of the claims newly added by the present amendment are patentable over the prior art, including Goodenough, on at least the same basis argued for the patentability of the aqueous biocidal solutions in the response submitted in the '890 application. Although Applicants expect that Examiner Pryor will be addressing Applicants' response submitted in the '890 application prior to examining the claims newly added by the present amendment, Applicants will repeat those arguments (along with submitting the same documentary evidence) in order to preserve Applicants' right to cite these documents in the event an appeal to the Board is required in the current application.

The claims added by the present amendment recite use of aqueous biocidal solutions which differ from the products described in the Goodenough patent. All of the newly added independent claims recite use of an "aqueous biocidal solution comprising at least 100,000 ppm (wt/wt) sulfamate stabilized halogen as measured as Br<sub>2</sub>, wherein the content of sulfamate stabilized halogen is" prepared or preparable by a method consisting of adding bromine chloride to an alkali metal sulfamate solution formed from water, sulfamic acid and alkali metal base, wherein the pH of said alkali metal sulfamate solution is maintained at about 13.0 or greater during bromine chloride addition, and wherein the molar ratio of sulfamic acid to bromine chloride is at least 0.93."

Applicants submit that the patentability of the newly added claims over Goodenough depends on whether the aqueous biocidal solutions recited in these claims are novel and nonobvious over Goodenough. Accordingly, to assist the Examiner in this assessment, Applicants direct the Examiner's attention to ¶¶ 1-12 of APPENDIX A (attached to the

current Response), which is titled Second Declaration of B. Gary McKinnie. This declaration was submitted during the interference in which the current application was previously involved (and labeled “Exhibit 1073” during that interference). In ¶¶ 4-12 of Appendix A, Dr. McKinnie discusses the results of studies conducted to determine the content of N-halosulfamate species present (specifically, N-bromosulfamate and N-chlorosulfamate) in an aqueous biocidal solution produced in a manner consistent with the preparation methods recited in the newly added independent claims. See, in particular, ¶ 4. In ¶¶ 5a-5e, Dr. McKinnie details the chemical test used to determine the presence and amounts of N-bromosulfamate and N-chlorosulfamate and the limitations of the method. In ¶¶ 6-8, Dr. McKinnie reports the results of laboratory experiments he personally conducted. Of particular note, in ¶ 6, Dr. McKinnie reports that addition of bromine chloride to an alkali metal sulfamate solution which was maintained at a pH of at least 13.0 during the addition of the bromine chloride resulted in an aqueous biocidal composition comprising an about 4: 1 molar ratio of stabilized bromine (i.e., N-bromosulfamate) to stabilized chlorine (i.e., N-chlorosulfamate).

Applicants submit that the experiments conducted by Dr. McKinnie clearly establish that the aqueous biocidal solution recited in the newly added independent claims contains both N-bromosulfamate and N-chlorosulfamate. If the Examiner is of the belief that the methods and results detailed by Dr. McKinnie are insufficient to establish this fact, the Applicants respectfully request that the Examiner state the specific basis on which that belief is founded.

In contrast to the mixed sulfamate stabilized halogen aqueous biocidal solutions called for in the newly added claims, Goodenough only describes methods for preparing N-bromosulfamate solutions. According to Goodenough, one method for preparing these solutions is to add bromine to an alkaline metal sulfamate solution. Goodenough further teaches that N-bromosulfamate solutions can be prepared even using as a starting material a brine solution containing sodium chloride or calcium chloride; however, there is no indication in Goodenough that N-chlorosulfamate would be produced. Applicants note that in order for N-chlorosulfamate to form in an alkali solution, chloride would first have to be oxidized to hypochlorite by bromine or hypobromite. Applicants are not aware of any scientific reference which indicates that this reaction can occur, and request that if the Examiner is aware of such a reference, that the Examiner provide such a source. Indeed,

Applicants are only aware of references which indicate that bromine is not a strong enough oxidizing agent to oxidize chloride ion to free chlorine. For example, Applicants direct the Examiner's attention to the following art teachings:

1. As noted at p. 1, lines 11-14 of the present application, prior art methods for producing hypobromite rely on the reverse reaction (i.e., on the oxidation of bromide to hypobromite by hypochlorite). See also, for example, U.S. Patent No. 5,476,670 (attached as APPENDIX B to the present Response), Abstract and col. 5, line 60 – col. 6, line 1.
2. Sea water, an exemplary chloride-containing brine solution, contains as much as 18 g/L of chloride only up to 65 mg/L of bromide ions. See Analytical Element Modeling of Coastal Aquifers, EPA/600/R-99/110 (January 2000), p. 1, lines 7-8 (relevant portion attached as APPENDIX C); and Harp, D.L., Current Technology of Chlorine Analysis for Water and Wastewater, Hach Technical Information Series – Booklet No. 17 (2002), page 12, col. 2, lines 17-18 (relevant portion attached as APPENDIX D). Notwithstanding the more than three orders of magnitude difference in chloride and bromide concentrations, it is known that hypochlorite generated by addition of chlorine to sea water reacts *irreversibly with bromide to form hypobromite*. *Id.*, page 12, col. 2, lines 18-23.

Applicants submit that the above references clearly indicate that addition of bromine to a brine solution containing sodium chloride or calcium chloride would not generate molecules comprising a chlorine atom having a 1+ oxidation state. Thus, even assuming for the sake of argument that some oxidizing chlorine atoms were generated during practice of the Goodenough method in a brine solution, the amount of such chlorine atoms would clearly be insufficient to generate an aqueous biocidal solution comprising detectable levels of N-chlorosulfamate. Since Dr. McKinnie's experiments indicate that the aqueous biocidal solutions recited in the newly added claims would have an about 4: 1 molar ratio of stabilized bromine (i.e., N-bromosulfamate) to stabilized chlorine (i.e., N-chlorosulfamate), no stabilized bromine solution preparable by any method described in the Goodenough patent anticipates the preparation or use of such aqueous biocidal solutions.



Moreover, as further elaborated below, it would not have been obvious to prepare (and therefore use) the recited aqueous biocidal solutions in view of Goodenough. The newly added independent claims recite use of an aqueous biocidal solution prepared or preparable by a process which differs from the process taught in the Goodenough patent in at least two respects: (1) use of bromine chloride instead of bromine; and (2) maintenance of a pH of about 13.0 or greater during bromine chloride addition versus sufficient hydroxide to provide for a final pH at the completion of bromine addition of between 8-10. See U.S. Patent 3,558,503, col. 2, lines 1-6. See also, col. 1, lines 69-72, and col. 5, lines 32-34. These two differences are in contrast to the interpretation given to previously pending claims 61-65 by the Board in their interference decision on rehearing (see Interference No. 105,223, paper 63, page 10, line 7 – page 11, line 5), and subsequently adopted by the Examiner, that is, that claims 61-65 read on a preparation method in which base is added subsequent to bromine addition to achieve a final pH of 13.0 or greater. While the Examiner's rejection of claims 61-65 relies upon the Dallmier patent (U.S. Patent No. 5,683,654) for providing a motivation to modify the Goodenough method to include a step of increasing the pH of the final solution, this combined teaching does not directly address the issue of whether it would have been obvious to add bromine or bromine chloride to an alkali metal sulfamate solution which *is maintained* at a pH of about 13.0 or greater. Thus, Applicants submit that no prima case of obvious exists as to the use of the aqueous biocidal solutions called for in the newly added independent claims.

As further elaborated below, even assuming for the sake of argument that one of skill in the art was motivated to modify the Goodenough process by substituting bromine chloride for bromine, such skilled artisan would not have maintained the pH of the alkali metal sulfamate solution at a pH of about 13.0 or greater during bromine chloride addition. As previously noted, the aqueous biocidal solutions called for in the methods of use recited in the newly added independent claims contain both N-chlorosulfamate and N-bromosulfamate. In contrast, the Goodenough patent teaches processes which seek to maximize the yield of N-bromosulfamate, and only N-bromosulfamate. A critical factor relied upon in prior art references which suggest the substitutability of bromine chloride and bromine is the rapid oxidation of bromide by hypochlorite (and hypochlorous acid). However, it was known in the art that the overall rate of oxidation of bromide by hypochlorite (and hypochlorous acid) is approximately six orders of magnitude slower at a pH of about 13 or greater in comparison

to the rate of oxidation at a pH of 7. See Kumar, K. et al., *American Chemical Society*, 26(16):2706-2711 (1987) (attached as APPENDIX N), page 2709, column 1, last paragraph and Figure 7. The difference in reaction rates is due to the fact that hypochlorite is  $1.5 \times 10^6$  times more reactive than hypochlorous acid in its reaction with bromide, and oxidation of bromide is largely driven by hypochlorous acid at high pH. *Id.*, page 2708, column 2.

The extremely slow rate of oxidation of bromide by hypochlorous acid (i.e., the mechanism of bromide oxidation which dominates at high pH) would have been an important consideration in any effort to modify the Goodenough process by substituting bromine chloride for bromine. In particular, it was known in the art at the date of the present invention that addition of a bromine stabilizer (such as sulfamic acid) prior to bromide oxidation would not permit the formation of hypobromous acid (or hypobromite). See U.S. Patent 5,795,487 (attached as APPENDIX G), col. 2, lines 60-65. Moreover, the Goodenough patent teaches more than one process for producing stabilized aqueous bromine solutions. In fact, Applicants note that the Goodenough patent broadly teaches that the order of addition of the three reactants (bromine, halogen stabilizer, and hydroxide) to water is not critical for producing stabilized aqueous bromine solutions. See Goodenough, col. 2, lines 7-12; and APPENDIX M, paragraph 100. Although the specific order of addition exemplified in the production of "Solution A" of Example 3 is relevant to the preparation method recited in the newly added claims, Example 3 of the Goodenough patent also exemplifies a process wherein hydroxide is added to a solution containing bromine and bromine stabilizer. Specifically, "Solution B" of Example 3 was prepared by adding magnesium hydroxide to a solution containing bromine and sulfamic acid. See Goodenough, col. 4, lines 69-72; and APPENDIX M, paragraph 101. In fact, Goodenough states that addition of hydroxide last (i.e., the order used to produce "Solution B") is the preferred manner of producing aqueous bromine solutions. See Goodenough, col. 5, lines 9-15.

In view of the art recognition that addition of a bromine stabilizer prior to bromide oxidation would not permit the formation of hypobromous acid (or hypobromite), one of skill in the art would not have had a reasonable expectation of avoiding side reactions (or maximizing the yield of N-bromosulfamate) using any one of the aqueous biocidal solution preparation methods recited in the newly added independent claims. Accordingly, Applicants submit that the preparation methods recited in the newly added independent claims would not have been obvious even over the combined teachings of Goodenough and Dallmier.

With respect to newly added independent claims 71, 91 and 96, which only call for an aqueous biocidal solution “preparable” by the recited method, Applicants submit that in view of the experiments conducted by Dr. McKinnie, it is clear that these claims call for use of an aqueous biocidal solution having sulfamate stabilized bromine (i.e., N-bromosulfamate) and sulfamate stabilized chlorine (i.e., N-chlorosulfamate). Accordingly, the aqueous biocidal solutions called for in each of the newly added independent claims differs from the aqueous N-bromosulfamate solutions described in Goodenough by the presence of N-chlorosulfamate. It follows that the proper inquiry under Section 103 for the newly added claims is whether in the first instance it would have been obvious at the time of the present invention to even prepare and use an aqueous biocidal solution comprising N-bromosulfamate and N-chlorosulfamate. As elaborated below, at the date of Applicants’ invention, one of skill in the art would not have been led to prepare and use, or seen any benefit in preparing and using, an aqueous biocidal solution comprising N-bromosulfamate and N-chlorosulfamate for use in microbiological control of cooling waters and disinfection of waste treatment systems.

Applicants first note that as of the date of Applicants’ invention, bromine based biocides (stabilized or unstabilized) were considered to have significant advantages over chlorine based biocides (stabilized or unstabilized) for microbiological control in water systems. See for example:

1. Page 1, lines 8-12 of the present application;
2. U.S. Patent 5,476,670 (attached as APPENDIX B, column 3, line 40 – col. 4, line 40;
3. U.S. Patent 5,516,501 (attached as APPENDIX E, column 1, lines 30-63 and column 2, lines 4-11;
4. U.S. Patent 3,316,173 (naming Mills and Goodenough as inventors) (attached as APPENDIX F, column 1, lines 19-72; and
5. U.S. Patent 5,795,487 (attached as APPENDIX G, column 1, lines 33-35; column 9, line 64 – column 10, line 4; column 11, line 38 – column 12, line 20; column 13, lines 19-59.

This preference of bromine over chlorine in the water treatment art specifically included a preference to use biocidal solutions containing N-bromosulfamate over biocidal solutions containing N-chlorosulfamate. See U.S. Patent 4,992,209 (attached as APPENDIX H, column 1, line 68 – column 2, line 2. As reflected in these references, there are many reasons

for the preference of bromine over chlorine. Consistent with this industry preference, Applicants were not aware prior to the work leading up to the present invention of any attempts in the water treatment industry to produce a stabilized mixed chlorine and bromine aqueous biocidal solution. Apparently others in the art were also not aware of any such attempts. Applicants note for example, U.S. Patent 7,045,153, having a filing date of June 2003 (and thus not prior art to the present application), states:

there is a need for [stabilized] liquid biocidal compositions based on mixtures of bromine and chlorine. No such compositions have ever been reported. All of the prior efforts have been directed toward the preparation of compositions in which bromine is the sole active ingredient, primarily because of the superior biocidal performance of bromine compounds compared to chlorine compounds.

See U.S. Patent 7,045,153 (attached as APPENDIX I), col. 4, lines 10-21.

Second, Applicants note that as of the date of the present invention, it was already appreciated by those of skill in the art that even among stabilized chlorine-based biocides, N-chlorosulfamate was considered a less effective biocide than other stabilized chlorine-based biocides. See U.S. Patent 5,565,109 (attached as APPENDIX J: column 1, lines 18-29; column 1, line 56 – column 2, line 2; column 2, line 60 – column 3, line 27; and Example 5 at columns 6-7). In fact, previous attempts to commercialize N-chlorosulfamate based biocides achieved very limited commercial success, presumably due to the weak biocidal activity of N-chlorosulfamate. See Urtz, B., Combined Halogens: New Products to Combat an Old Problem, Solutions! (Attached as APPENDIX K), page 1, paragraph 4.

It follows from the above that even assuming for the sake of argument that one of skill in the art had contemplated producing an aqueous biocidal solution comprising a stabilized chlorine compound in addition to a stabilized bromine compound (such as N-bromosulfamate), the skilled artisan, expecting the two halogen compounds to only have an additive effect at best, would have had ample reason to select a stabilized chlorine compound other than N-chlorosulfamate. Subsequent to the date of the present invention, however, and contrary to the teachings in the art, it has been determined that even in highly dilute concentrations, such as those encountered following addition of bromide and N-chlorosulfamate to a water system, N-chlorosulfamate oxidizes bromide to form hypobromous acid (BrOH) and hypobromite (BrO<sup>-</sup>) and possibly N-bromosulfamate. See, for example:

1. U.S. Patent 6,478,972 (attached as APPENDIX L), having a filing date of June, 2000 (and thus not prior art to the present application), column 2, line 61 – column 3, line 11; column 6, lines 1-41; column 7, lines 23-30; and Examples 1-4 at columns 8-11;
2. U.S. Patent 7,045,153 (attached as APPENDIX I), having a filing date of June 2003 (and thus not prior art to the present application), column 10, line 54 – column 11, line 4; and
3. U.S. Patent 6,669,904 (attached as APPENDIX O), having a filing date of August, 2001 (and thus not prior art to the present application), Example 2 at column 4.

In addition, Applicants note that it is well known in the art that in the process of killing microorganisms or oxidizing organic material, hypobromous acid is reduced to form bromide ion. See, for example, U.S. Patent 5,476,670 (attached as APPENDIX B), col. 6, lines 3-9. Since the aqueous biocidal solutions called for in the newly added claims comprise N-chlorosulfamate, and in use generate bromide ions (following reduction of hypobromite originating from N-bromosulfamate), it follows that the aqueous biocidal solutions when used as claimed would exhibit an extended residual biocidal activity (in comparison to Goodenough's biocidal solutions which only contain N-bromosulfamate) consistent with the phenomena described in U.S. Patent 6,478,972 and U.S. Patent 6,669,904. Moreover, because the ability of N-chlorosulfamate to oxidize bromide to form hypobromous acid in highly dilute concentrations, such as those encountered following addition of bromide and N-chlorosulfamate to a water system, was not known as of the date of the present invention, the extended residual biocidal activity represents an unexpected property of the aqueous biocidal solutions present when used as claimed.

Finally, Applicants respectfully wish to convey to the Examiner that as per the MPEP, the fact that the unexpected property of extended residual biological activity of the claimed aqueous biocidal solutions in use is not disclosed in the specification does not mean the Examiner can discount the above evidence and arguments, where as here, the unexpected property inherently flows from its disclosed use for the microbiological control of cooling waters and disinfection waste treatment systems. See MPEP 716.02(f) (citing *In re Zenitz*, 333 F.2d 924, 928, 142 USPQ 158, 161 (CCPA 1964) (evidence that claimed compound

minimized side effects of hypotensive activity must be considered because this undisclosed property would inherently flow from disclosed use as tranquilizer).

In view of the above arguments, Applicants submit that all of the newly added claims are clearly patentable over the prior art. Consideration and allowance are respectfully solicited.

If matters remain requiring further consideration, the Examiner is respectfully requested to telephone the undersigned so that such matters may be discussed and, if possible, can be promptly resolved.

Respectfully submitted,  
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# APPENDIX

## A

## **SECOND DECLARATION OF B. GARY McKINNIE**

I, B. Gary McKinnie, declare as follows:

1. I am the same B. Gary McKinnie who provided a previous declaration for interference nos. 105,222, 105,223 and 105,230.
2. I have held various technical titles within Ethyl / Albemarle Corp. (Chemist, Senior chemist, Specialist, Senior Specialist, Advisor, Senior Advisor) and in 2000 was promoted to Distinguished Advisor.
3. Since 1983 I have conducted research and development of processes for producing bromine, brominated flame retardants and other bromine-related products. Since 2000 I have carried out research and development work on processes for making bromine-based biocides.
4. In 2000 as part of my research duties at Albemarle I personally conducted lab experiments to determine the N-halo compound make-up (specifically, the presence of N-bromosulfamate and N-chlorosulfamate) of a biocide solution which results from adding bromine chloride (pre-prepared or made inline) to an aqueous alkali metal sulfamate solution formed from water, sulfamic acid and sodium hydroxide (an alkali metal base). I also experimented adding bromine first, then chlorine, to the same aqueous alkali metal sulfamate solution.
5. The method used to determine the presence of N-halo compounds in the resulting composition was as follows.
  - a. Hach Company (Loveland, CO) has two color tests developed to measure "free chlorine" and "total chlorine" in water at the few part per million (ppm) level. It is based on the chlorine oxidation of N,N-diethyl-p-



## SECOND DECLARATION OF B. GARY McKINNIE

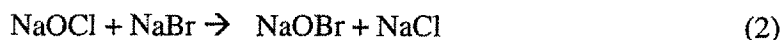
I, B. Gary McKinnie, declare as follows:

1. I am the same B. Gary McKinnie who provided a previous declaration for interference nos. 105,222, 105,223 and 105,230.
2. I have held various technical titles within Ethyl / Albemarle Corp. (Chemist, Senior chemist, Specialist, Senior Specialist, Advisor, Senior Advisor) and in 2000 was promoted to Distinguished Advisor.
3. Since 1983 I have conducted research and development of processes for producing bromine, brominated flame retardants and other bromine-related products. Since 2000 I have carried out research and development work on processes for making bromine-based biocides.
4. In 2000 as part of my research duties at Albemarle I personally conducted lab experiments to determine the N-halo compound make-up (specifically, the presence of N-bromosulfamate and N-chlorosulfamate) of a biocide solution which results from adding bromine chloride (pre-prepared or made inline) to an aqueous alkali metal sulfamate solution formed from water, sulfamic acid and sodium hydroxide (an alkali metal base). I also experimented adding bromine first, then chlorine, to the same aqueous alkali metal sulfamate solution.
5. The method used to determine the presence of N-halo compounds in the resulting composition was as follows.
  - a. Hach Company (Loveland, CO) has two color tests developed to measure "free chlorine" and "total chlorine" in water at the few part per million (ppm) level. It is based on the chlorine oxidation of N,N-diethyl-p-

phenylenediamines (DPD) to a Wurster dye that is highly colored, the intensity of which is proportional to the amount of oxidation that has occurred. **EXHIBIT 1074**, p. 2, col. 2, ¶¶ 1-2.

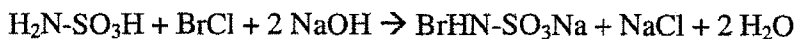
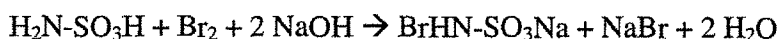
- b. N-chloro compounds are very slow to oxidize DPD but in the presence of a trace of iodide the oxidation does occur rapidly. **EXHIBIT 1074**, p. 3, col. 1, ¶ 1.
  - c. While N-chloro compounds are very slow to oxidize DPD in the absence of iodide, N-bromo compounds do oxidize DPD in the absence of iodide.
  - d. Thus, carrying out the analysis in the absence of iodide gives the quantity of N-bromo compound. Repeating the analysis in the presence of iodide gives the total oxidant level, which is a measure of both the N-bromo and N-chloro compounds. The ratio of the N-bromo to total oxidant level represents the mole fraction of N-bromo compounds present in the final biocide solution.
  - e. One limitation of the above method is that since the test relies upon the slow reaction of N-Cl with DPD in the absence of iodide, the accuracy of the test when a large ratio of the N-halo compound is N-chloro (say 50% or more) can result in an erroneously high reading of N-bromo compound.
6. When the pH of the aqueous alkali metal sulfamate solution prior to bromine chloride addition has a pH above 13, and upon simultaneous addition of bromine chloride with sodium hydroxide in order to maintain the pH above 13, only about 80 mole % of the N-halo sulfamate compound formed was N-bromosulfamate. The remaining about 20 mole % N-halo compound formed was N-chlorosulfamate. Similar results were achieved regardless of whether the bromine chloride was pre-prepared or made inline.

7. The above results were consistent with the fact that bromine chloride exists as an equilibrium mixture of 20 mole % Br<sub>2</sub>, 20 mole % Cl<sub>2</sub>, and 60 mole % BrCl.
8. By contrast, keeping the other conditions the same, but instead of using BrCl, adding first bromine, then an equal amount of chlorine, only about 60 mole % of the N-halo sulfamate solution formed was N-bromosulfamate.
9. These differences in results demonstrate there is little or no oxidation of bromide to bromine by chlorine (reaction (1), below) or to hypobromite by hypochlorite (reaction (2), below) (either of which if occurred would prevent formation of N-chlorosulfamate), nor is there an N-chloro to N-bromo exchange occurring at pH above 13 (reaction (3), below). In other words, the following reactions do not occur at pH above 13:

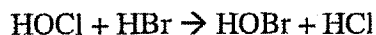


Had any of these reactions occurred, then there would be no difference in using bromine or BrCl as the final percentage of N-bromosulfamate would have been about the same in both sets of experiments.

10. In summary, the overall reactions believed to occur upon bromine chloride addition to an alkali metal sulfamate solution at high pH are believed to be as follows:



11. The fact that reaction (2) (paragraph 9, above) does not occur at high pH is in contrast to what occurs at neutral pH. Specifically, the oxidation of bromide via the reaction:



is known to occur fairly rapidly in water at neutral pH. **EXHIBIT 2011**, p. 8 (cover counted as page 1), last paragraph. Accordingly, in water, bromine chloride appears to hydrolyze completely to hypobromous acid (HOBr). *Id.*

12. To my knowledge, the fact that oxidation of bromide does not occur at high pH, as demonstrated by the above experiments, was not known in the art prior to 2000.

Accordingly, I had no expectation prior to performing the above experiments that use of bromine chloride in the process would not be equivalent to using bromine. For the same reason, I also did not have any reason to expect that the process would be equivalent to using bromine.

13. Count 1 of Interference No. 105,230 is identical to claim 1 of Yang's U.S. Patent No. 6,287,473. Count 1 of Interference No. 105,222 is identical to claim 14 of Yang's U.S. Patent No. 6,423,267. I have been instructed by Moore's attorney's to interpret the scope of these counts in a manner which is consistent with the patent from which each count originates.

- a. As noted in my first declaration, one of skill in the art would interpret the "caustic solution" recited in claim 1 of the '473 patent and claim 14 of the '267 patent as having a pH higher than 14. **EXHIBIT 1001**, ¶¶ 44, 44(b), 93, and 93(b).

- b. Accordingly, one of skill in the art would interpret the "caustic solution" recited in Count 1 of the '222 interference and Count 1 of the '230 interference as having a pH higher than 14.
  - c. In view of the results of the experiments described above (¶¶ 4-10), I would expect that the immediate product of the process steps recited in Count 1 of the '230 interference, wherein sulfamic acid is used as the halogen stabilizer, to be a composition comprising N-bromosulfamate, N-chlorosulfamate, a bromide salt (for example, NaBr), and a chloride salt (NaCl). The composition could further comprise N,N-dibromosulfamate, N-bromo-N-chlorosulfamate, and N,N-dichlorosulfamate.
  - d. I would expect that the immediate product of the process steps recited in Count 1 of the '222 interference, wherein sulfamic acid is used as the halogen stabilizer, to be a composition comprising N-bromosulfamate and a bromide salt. The composition could further comprise N,N-dibromosulfamate.
14. Thus the immediate composition which results from the process recited in Count 1 of the '230 interference would contain the additional compounds N-chlorosulfamate and a chloride salt. The composition may further differ by containing N-bromo-N-chlorosulfamate, and N,N-dichlorosulfamate.
15. I have reviewed the Declarations of Dr. Shunong Yang, Dr. Jack Mills, and John A. Wojtowicz.
16. At ¶¶ 47-53 of the Yang Decl., Dr. Yang cites a number of references for the proposition that bromine and bromine chloride are interchangeable in the process recited in Count 1 of the '222 interference.

- a. The first reference, cited in ¶ 47, is Moore's U.S. Patent No. 6,068,861, col. 1, ll. 28-67. This section of the '861 patent describes the recognition in the art that both bromine and bromine chloride could be used as a biocide by direct introduction into a water system.
- b. The second reference, cited in ¶¶ 48-49, is a paper titled "The Chemistry of Bromine Chloride in Waste Water Disinfection." **EXHIBIT 2009**, p. 1. This reference only relates to the direct use of bromine chloride for wastewater treatment as a substitute for either bromine or chlorine. See, for example, **EXHIBIT 2009**, p. 6, "Conclusion".
- c. The third reference, cited in ¶ 50, is a product bulletin published by Dow Corporation. **EXHIBIT 2010**. This reference proposes bromine chloride as a viable alternative to chlorination for industrial cooling water systems. See, for example, **EXHIBIT 2010**, p. 1, col. 1, ¶ 1 and col. 2, ¶¶ 1-2 (not including bullet points).
- d. The fourth reference, cited in ¶ 51, is a brochure published by the Ethyl Corporation. **EXHIBIT 2011**. Similar to the above two references, the brochure advocates the advantages of using directly using bromine chloride over chlorine in water treatment. **EXHIBIT 2011**, p. 2 (counting cover as p. 1).

17. All of the references cited by Dr. Yang relate to use of bromine chloride in water treatment. Industrial water systems generally have a pH between 7 and 9. Thus the similarity in reactions which bromine and bromine chloride undergo in a water

system having a pH in this range cannot be predictably extrapolated to the high pH conditions called for in the “caustic solution” of Count 1 of the ‘222 interference.

18. At ¶ 47 of the Mills Decl., Dr. Mill cites his own paper (**EXHIBIT 2014**) for the proposition that in most bromination reactions, bromine chloride could be used instead of bromine. Thus, Dr. Mill asserts, it would have been obvious to use bromine chloride instead of bromine in the process recited in Count 1 of the ‘222 interference.

- a. Consistent with what was known in the art (see ¶ 11, above) Dr. Mills paper teaches that upon to addition to water (pH ~ 7), any bromide formed upon addition of BrCl to water would quickly be oxidized via the reaction:



**EXHIBIT 2014**, p. 164, col. 2, section on “Reactions of Bromine Chloride with Water”.

- b. I have reviewed **EXHIBIT 2014** and would agree with Dr. Mills that bromine chloride could be used as a substitute for bromine in the reactions discussed in this reference.
- c. However, the process recited in Count 1 of the ‘222 interference is not discussed in Dr. Mills paper. Further, nothing in the paper suggests that bromine chloride and bromine are equivalent at the high pH called for in the “caustic solution” of Count 1 of the ‘222 interference.

19. As noted Dr. Mills paper, chlorination side reactions represented a significant concern since BrCl exists in an equilibrium mixture containing Br<sub>2</sub> and Cl<sub>2</sub>. **EXHIBIT 2014**, p. 160, col. 2, last paragraph. In my opinion, Dr. Mills paper would not have

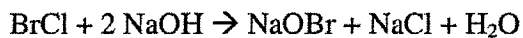
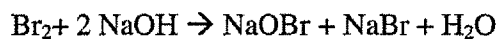
suggested to one of skill in the art that N-chloro compounds would not be produced using bromine chloride under the high pH conditions called for in the “caustic solution” of Count 1 of the ‘222 interference or that the levels of N-bromo compounds would be equivalent to using bromine in the process.

20. At ¶¶ 49-54 of the Wojtowicz, Mr. Wojtowicz cites a number of references for the proposition that the substitution of bromine chloride in the process recited in Count 1 of the ‘222 interference would have been obvious.

- a. Based on my reading of these paragraphs, Mr. Wojtowicz fails to account for the fact that bromine chloride contains around 20% bromine, around 20% chlorine, and around 60% BrCl.
- b. Therefore, ¶ 50 of the Wojtowicz Decl., which asserts that both Br<sub>2</sub> and BrCl contain the same molar amount of “available bromine” (i.e., bromine in the +1 oxidation state) is factually incorrect. One mole of BrCl would only contain 0.8 moles of available bromine, whereas Br<sub>2</sub> would contain 1 mole of available bromine.
- c. Similarly, ¶¶ 51-52 of the Wojtowicz Decl., which compares the reactions of single Br<sub>2</sub> and BrCl molecules with base, fails to account for the fact that liquid bromine chloride comprises around 20% bromine and around 20% chlorine. Accordingly, ¶¶ 51-52 of the Wojtowicz Decl. are not predictive of the composition which results from substitution of bromine chloride for bromine under the high pH conditions called for in the “caustic solution” of Count 1 of the ‘222 interference.



- d. Since liquid bromine chloride contains around 20% bromine and around 20% chlorine, the following reactions would be expected to occur upon addition of bromine chloride to an aqueous base (NaOH) solution:



I hereby declare under penalty of perjury that all of the statements made by me herein are true.

Date: *Feb. 14, 2005*

*B. Gary McKinnie*  
B. Gary McKinnie

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# APPENDIX

## B



US005476670A

**United States Patent** [19]**Hight et al.**[11] **Patent Number:** **5,476,670**[45] **Date of Patent:** **Dec. 19, 1995**[54] **BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMS**[75] **Inventors:** Terry V. T. Hight; Jack V. Matson, both of Houston, Tex.; Lawrence F. Rakestraw, Chesterfield, Mo.; Zhihe Zhang, Houston, Tex.; Thomas C. Kuechler, St. Louis, Mo.[73] **Assignee:** The University of Houston, Houston, Tex.[21] **Appl. No.:** 259,327[22] **Filed:** Jun. 13, 1994**Related U.S. Application Data**

[63] Continuation of Ser. No. 212,287, Mar. 14, 1994, Pat. No. 5,464,636, which is a continuation of Ser. No. 750,744, Aug. 21, 1991, abandoned, which is a continuation of Ser. No. 366,936, Jun. 16, 1989, abandoned.

[51] **Int. Cl.**<sup>6</sup> ..... A01N 59/08; A01N 59/00; A01N 43/66; A01N 43/50[52] **U.S. Cl.** ..... 424/661; 424/723; 514/241; 514/389; 514/401; 514/402[58] **Field of Search** ..... 424/661, 723; 514/241, 401, 402, 389[56] **References Cited****U.S. PATENT DOCUMENTS**

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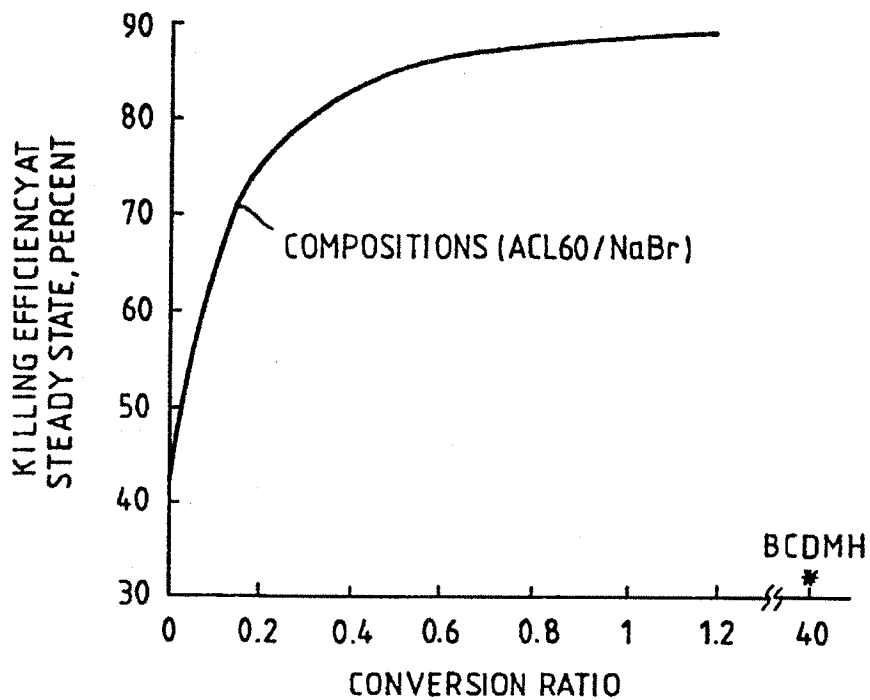
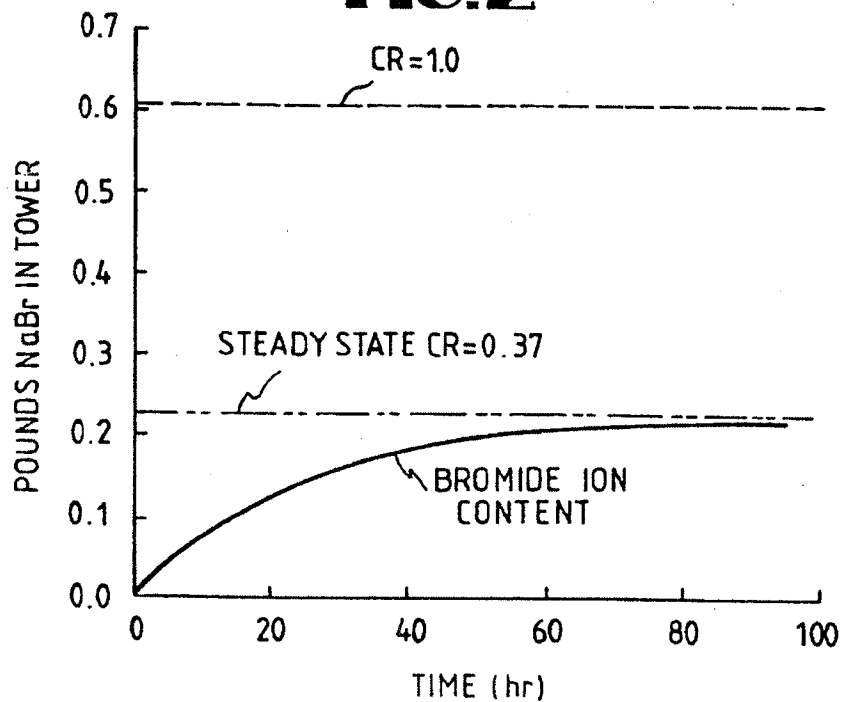
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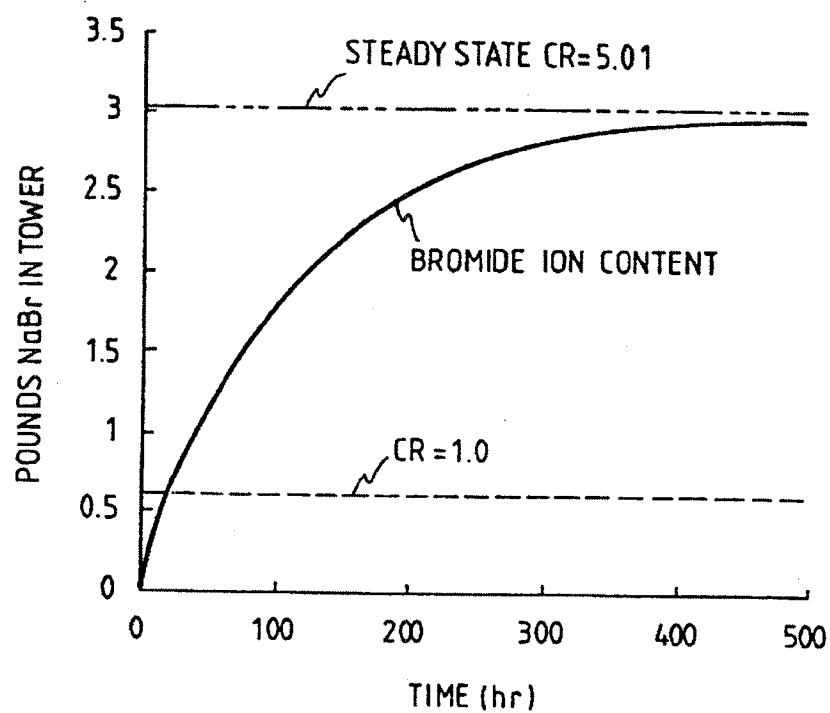
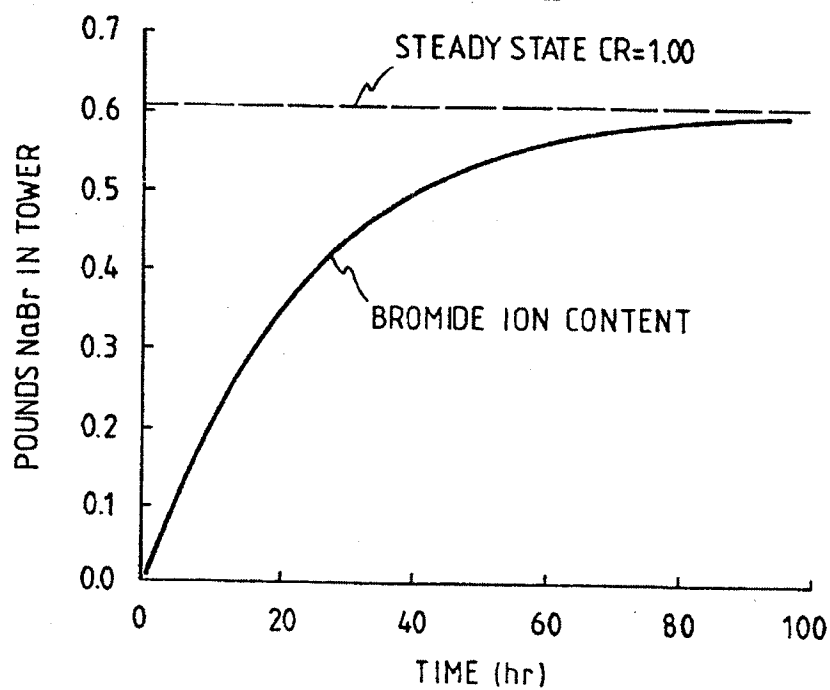
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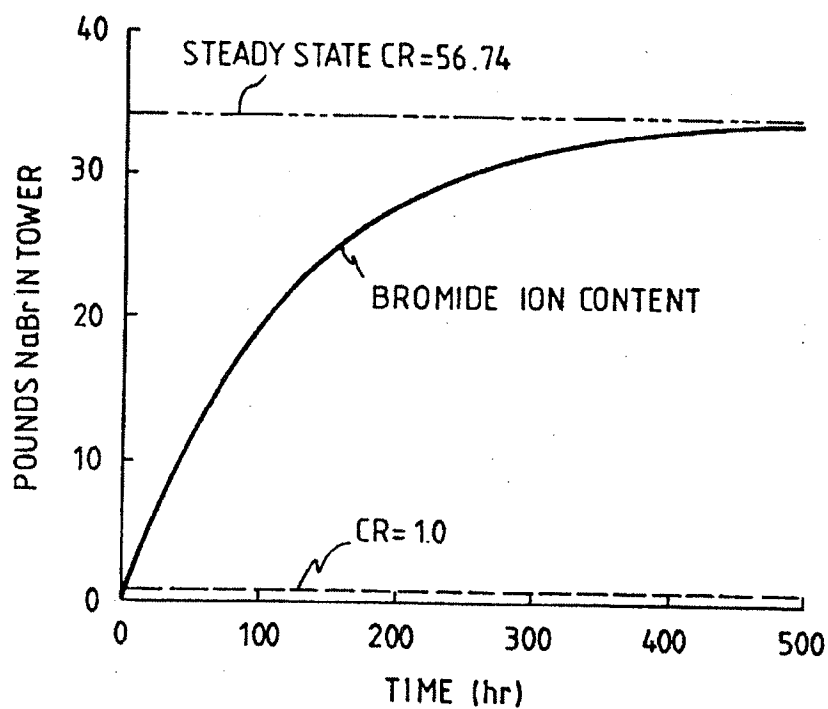
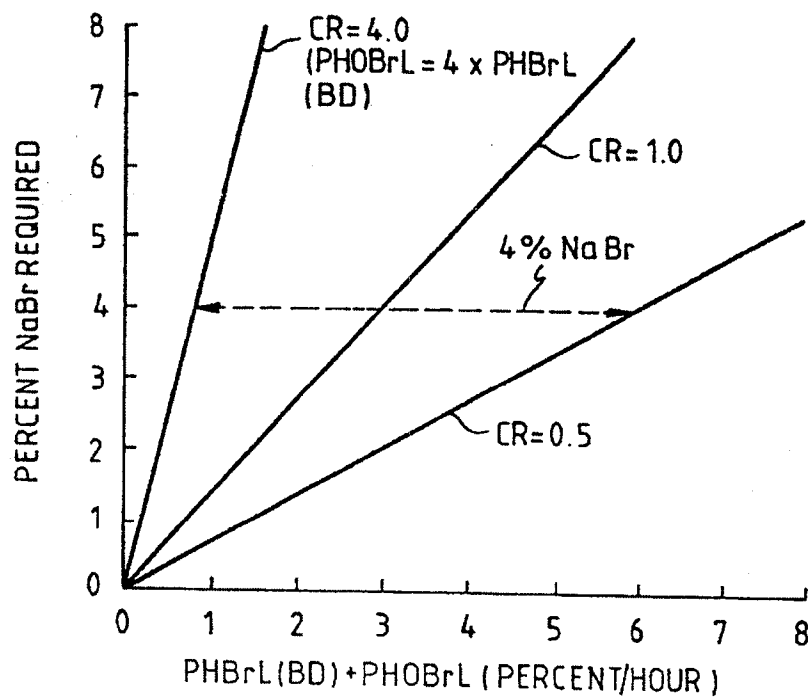
*Primary Examiner*—Raymond Henley, III*Assistant Examiner*—Kevin F. Weddington[57] **ABSTRACT**

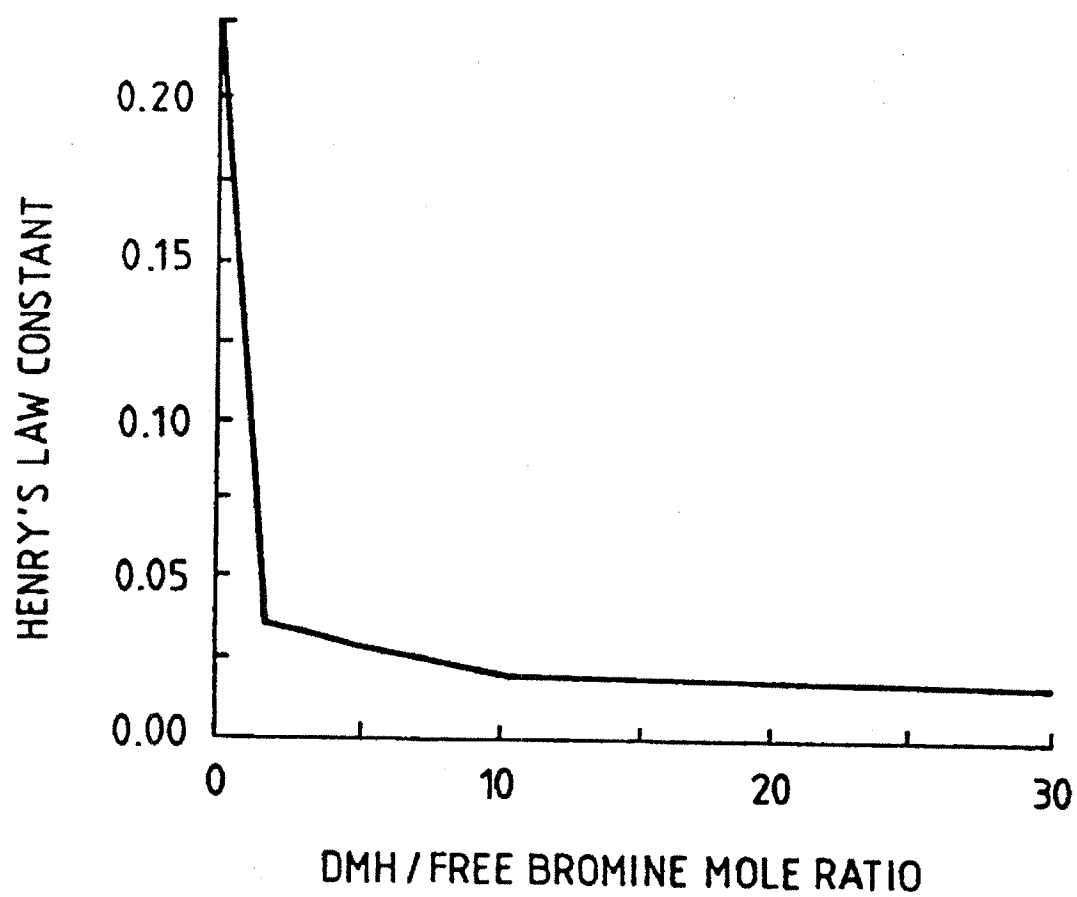
Improved biocidal composition and method for controlling biofouling and microorganism population levels in recirculating water systems such as cooling towers, swimming pools or spas is disclosed and claimed. The composition comprises a hypochlorite donor and a bromide ion donor in proportions selected to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20. The method comprises introducing into the recirculating water a mixture or combination of a hypochlorite donor and a bromide ion donor in an amount sufficient to maintain a ratio of the sum of all bromine containing species to the sum of all species in the recirculating water in the range of about 0.2 to about 20. In addition, a bromine volatilization suppressant may be introduced into the recirculating water to inhibit loss of bromide ion through volatilization of bromine containing species formed by reaction of the hypochlorite donor and the bromide ion donor. One or more scale inhibitors and compacting aids may also be added.

**28 Claims, 4 Drawing Sheets**

**FIG. 1****FIG. 2**

**FIG. 3****FIG. 4**

**FIG. 5****FIG. 6**

**FIG.7**

## BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMS

This application is a continuation of application Ser. No. 08/212,287, filed Mar. 14, 1994, now U.S. Pat. No. 5,464,636, which is a continuation of application Ser. No. 07/750,744, filed Aug. 21, 1991, now abandoned; which is a continuation of 07/366,936, filed Jun. 6, 1989, now abandoned.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to the disinfection of water and to the control of biofouling in recirculating water systems such as cooling towers, evaporative condensers, air washers, swimming pools, hot tubs, and spas.

The invention more especially concerns methods and compositions for controlling biofouling and microorganism population levels in such systems wherein water soluble hypochlorite donors and bromide ion donors are added to the systems so as to improve biocidal effectiveness with reduced costs.

As used herein, the term "hypochlorite donor" means any compound that will generate hypochlorite species when dissolved in water.

The term "bromide ion donor" means any compound that will generate bromide ions when dissolved in water.

The term "available halogen" means the standard form for expressing the strengths or capacities of halogenating chemicals as well as for the doses in which they are applied and for the hypohalite species ( $\text{HOCl}$ ,  $\text{OCl}^-$ ,  $\text{HOBr}$ ,  $\text{OBr}^-$ ) which remain in the water.

The term "available chlorine" means the same as "available halogen", but refers specifically to chlorine compounds.

The term "available bromine" means the same as "available halogen", but refers specifically to bromine compounds.

The term "hypohalite species" means hypochlorous acid, hypochlorite ion, hypobromous acid and hypobromite ion.

The term "hypochlorite species" means hypochlorous acid and hypochlorite ion.

The term "hypobromite species" means hypobromous acid and hypobromite ion.

The term "bromine species" means hypobromous acid, hypobromite ion, and bromide ion.

The terms "free halogen" and "free available halogen" are used interchangeably and are defined as the concentration of halogen existing in the water as hypohalous acid,  $\text{HOX}$ , and hypohalite ion,  $\text{OX}^-$ , where X is Cl or Br.

The terms "free chlorine" and "free available chlorine" are used interchangeably and are defined as the concentration of chlorine existing in the water as hypochlorous acid,  $\text{HOCl}$ , and hypochlorite ion,  $\text{OCl}^-$ .

The terms "free bromine" and "free available bromine" are used interchangeably and are defined as the concentration of bromine existing in the water as hypobromous acid,  $\text{HOBr}$ , and hypobromite ion,  $\text{OBr}^-$ .

The terms "combined halogen" and "combined available halogen" are used interchangeably and are defined as the concentration of halogen existing in the water in chemical combination with ammonia or organic nitrogen compounds.

The terms "combined chlorine" and "combined available chlorine" are used interchangeably and are defined as the concentration of chlorine existing in the water in chemical combination with ammonia or organic nitrogen compounds. The terms "combined bromine" and "combined available bromine" are used interchangeably and are defined as the

concentration of bromine existing in the water in chemical combination with ammonia or organic nitrogen compounds.

The terms "total halogen" and "total available halogen" are used interchangeably and are defined as the sum of "free halogen" (or "free available halogen") and "combined halogen" (or "combined available halogen").

The terms "total chlorine" and "total available chlorine" are used interchangeably and mean the same as "total halogen" and "total available halogen" but specifically refer to chlorine.

The terms "total bromine" or "total available bromine" are used interchangeably and mean the same as "total halogen" and "total available halogen" but specifically refer to bromine.

The symbol "FAvC" represents "free chlorine" and "free available chlorine" concentrations in the water.

The symbol "AvC" represents the available chlorine content of the hypochlorite donor.

The term "halogen demand" is defined as the amount of halogen which must be added to the water over a specific period of time to maintain the "free halogen" and/or "free available halogen" at a specific concentration in the water.

The term "chlorine demand" means the same as the "halogen demand" but specifically refers to "free chlorine" and/or "free available chlorine" concentrations.

The term "chlorinated isocyanuric acid derivative" means chlorinated isocyanuric acid including dichlorinated and trichlorinated isocyanuric acid, alkali metal and alkaline earth metal salts of chlorinated isocyanuric acid, and hydrates, complexes and mixtures thereof.

The term "hydantoin derivative" means an unsubstituted, halogenated (i.e. chlorinated or brominated), or alkylated hydantoin.

The term "sulfamic acid derivative" means unsubstituted, halogenated, or alkylated sulfamic acid.

The term "sulfonamide derivative" means halogenated, alkylated, or arylated sulfonamide.

The term "glycoluril derivative" means unsubstituted, halogenated, or alkylated glycoluril.

The term "succinimide derivative" means unsubstituted, halogenated, or alkylated succinimide.

The term "oxazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated oxazolidinone.

The term "imidazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated imidazolidinone.

The term "halogen concentration (free chlorine basis or free available chlorine basis)" means the halogen concentration in terms of free available chlorine, regardless of whether the halogen species are hypochlorite, hypobromite or mixtures thereof.

#### 2. Related Art

Cooling towers are used to provide cooling for the air conditioning systems of office buildings, hotels and hospitals and to provide cooling for industrial processes. The water in these towers is subject to contamination from the air blown through the tower and from the fresh water used to compensate for evaporative losses and blowdown. The contamination consists of both inorganic and organic debris as well as live microorganisms capable of growing and multiplying if suitable conditions are provided. Formation of microbial deposits, known as biofouling, can occur on almost any surface exposed to an aqueous environment, causing substantial energy losses due to increased heat transfer resistance. For this and other reasons, cooling



towers are adversely affected by microorganisms, e.g. bacteria, fungi, molds, and algae, by either sheer numbers of organisms, metabolic waste products generated, health hazards presented, or deposits created. Unfortunately, cooling towers provide many of the conditions ideal for microbial growth, namely favorable temperatures and moisture levels, and favorable concentrations of air and nutrients.

Air washers are used to cool, cleanse, and humidify the air in office buildings, factories, shopping malls, and the like. Due to the large amount of air drawn through the water, the growth of microorganisms is again a problem. Since the air is used directly for inhabited areas, the toxicity and odor of any compounds used for treatment of the water in the air washers must be extremely low.

Similarly, water in swimming pools, hot tubs and spas must be sanitized in order to control disease spreading microorganisms. As with air washers, the toxicity and odor of compounds used to treat the water must be extremely low.

It is customary to treat biologically contaminated water with one or more biocides to control the population of microorganisms in the water, to prevent fouling of heat exchanger surfaces, and to prevent the spread of disease. The biocides most commonly used to disinfect and sanitize water in recirculating water systems are chemicals that generate hypochlorite species when dissolved in water. There are many hypochlorite generating chemicals, but the more common ones are chlorine gas, alkali metal hypochlorites such as sodium hypochlorite, alkaline earth metal hypochlorites such as calcium hypochlorite, chlorinated hydantoins, and chlorinated isocyanuric acid derivatives.

Dry sources of biocide are often preferable to gaseous or even liquid forms because the dry forms are often safer to handle, more convenient to store and use, and more stable in storage. Moreover, one or more dry products may conveniently be fed to a recirculating water system using an erosion feeder in which water is passed through a bed of solid biocide to slowly dissolve the biocide and is then added to the recirculating water. One such erosion feeder is described in U.S. Pat. No. 3,412,021.

The different forms of hypochlorite donors all work by generating hypochlorous acid (HOCl) in solution, which provides the significant biocidal action. Hypochlorous acid has strong biocidal properties under the proper conditions. Its killing power is adversely affected, however, by alkaline pH levels and by the presence of ammonia or other nitrogenous material.

The pH of cooling water is typically regulated in the range of 8.0 to 9.0 for alkaline corrosion protection. At pH levels above 7.5, chlorine-based biocides become less effective because of the equilibrium shift from hypochlorous acid to hypochlorite ion.



$$pK = -\log \left[ \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} \right] = 7.5 \text{ (at } 20^\circ \text{ C.)}$$

The hypochlorite ion cannot easily penetrate microorganism cell membranes, while the uncharged hypochlorous acid can passively diffuse into cells to cause damage.

Water in recirculating water systems is also frequently contaminated with ammonia due to the decomposition of nitrogenous impurities in the water or to the leakage of ammonia from refrigeration units into the cooling water. Ammonia or chloramines are also commonly introduced into the recirculating water system by the makeup water.

Hypochlorite species react with ammonia to form chloramines. Since chlorine is bound very strongly by nitrogen, the chlorine is not readily released by chloramines to the water as hypochlorite species, and the biocidal activity of the chlorine-based biocide is, therefore, greatly reduced. The fact that the chloramines are relatively stable chlorine compounds also makes it more difficult for some cooling tower systems to comply with the EPA total halogen (free halogen+combined halogen) discharge limit of 0.2 ppm. In some cases, these cooling tower systems frequently have to dechlorinate the discharge water in order to be in compliance. Moreover, chloramines have a disagreeable and irritating odor. They can be converted to odorless nitrogen gas by maintaining the appropriate free chlorine concentration in the recirculating water, but some chloramines are still volatilized into the air. Even though the amounts are negligible, chloramine odors are still noticeable. Chloramine odor is an important issue with indoor pools and spas because the air containing the volatilized chloramines is retained in the buildings long enough for the chloramine concentration to accumulate to levels that are objectionable to the consumer. Thus, the formation of chloramines in recirculating water can present a serious obstacle to the use of chlorine-based biocides.

Hypobromous acid (HOBr), which can be generated from a number of compounds including liquid bromine and N-bromo organic compounds or by reacting a bromide salt with a solution of hypochlorous acid or other oxidizing agents, is a more effective biocide on a molar basis than hypochlorous acid. Under some conditions, this superiority is quite dramatic. In particular, hypobromous acid is known to react with ammonia to produce bromamines. Bromamines, unlike chloramines, have very good biocidal activity and have a more acceptable odor. Bromamines also have a distinct advantage over chloramines because they dissipate more readily, thereby making it easier to operate cooling towers in compliance with the ERA limits for total halogen. In addition, hypobromite species are more effective than hypochlorite species at pH values above 7.5 due to the higher pK value for the equilibrium shift from hypobromous acid to hypobromite ion.



$$pK = -\log \left[ \frac{[\text{OBr}^-][\text{H}^+]}{[\text{HOBr}]} \right] = 8.5 \text{ (at } 20^\circ \text{ C.)}$$

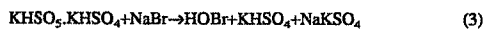
In most cases where hypobromous acid is used as a biocidal agent, the hypobromous acid generating composition contains a large weight percentage of bromine. Liquid bromine, for example, is 100% bromine by weight and 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) is 32.8% bromine by weight. This practice leads to higher costs for the bromine-based biocides since the cost of bromine is about three times the cost of chlorine per pound. Since 2.25 pounds of bromine contain the same number of moles of available halogen as only 1.0 pound of chlorine, bromine is over seven times more expensive than chlorine on a per mole basis. Even though hypobromous acid is generally superior to hypochlorous acid, the higher cost of bromine has limited the use of bromine-based biocides.

Nevertheless, in the past few years several products have been introduced into the cooling tower marketplace which take advantage of the bromine chemistry. In 1982, Nalco introduced a bromine-based product (tradename Actibrom) for use in large scale cooling towers. These towers already had chlorinators injecting gaseous chlorine for disinfection.

Actibrom is simply an aqueous solution of sodium bromide, and is typically added in proportion to the chlorine gas using a separate feeder. See U.S. Pat. No. 4,451,376. Another bromine-based biocide, 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) was introduced into the cooling tower marketplace by Great Lakes Chemical. See U.S. Pat. No. 4,297,224.

Bromine sanitizers have also gained some measure of popularity for indoor pool and spa applications, because the odor of the bromamines, formed by reaction of hypobromite species with nitrogenous wastes, is less objectionable to the consumer. Bromine sanitizers, however, have not been popular for outdoor pools because the hypobromite species are rapidly dissipated in sunlight and the sanitizer costs are considerably higher than chlorine sanitizers with cyanuric acid.

Potassium monopersulfate and sodium bromide have been marketed together as a bromine sanitizer system for spa applications. The recommended practice is to dose the spa water with sodium bromide (usually as a solution) and then add the recommended dosages of potassium monopersulfate as needed. Hypobromous acid is generated by oxidation of the bromide ion with persulfate ions as shown by the following equation:



Currently available dry sources of hypobromous acid suffer from a number of disadvantages in addition to their higher cost. The hydantoin products such as BCDM, 1,3-dichloro-5,5-dimethylhydantoin (CCDMH), 1,3-dibromo-5,5-dimethylhydantoin (BDDMH), 1,3-dichloro-5-ethyl-5-methylhydantoin (CCEMH), and 1-bromo-3-chloro-5-ethyl-5-methylhydantoin (BCEMH) have very low dissolution rates which necessitates the use of large feeder systems and high water flow rates. Moreover, in some cases it is desirable to add a large amount of available halogen at one time to rapidly clean up a recirculating water system. This is known as a "shock treatment". Such a treatment would be desired whenever a system has experienced a large amount of contamination or when microorganism growth has gotten out of control. However, the hydantoin products are generally unsuited for this application due to their low dissolution rates.

In addition, the hydantoin products are not as effective biocides as might be expected based on the amount of hypobromous acid formed, because these products also release large amounts of 5,5-dimethylhydantoin (DMH) or 5-ethyl-5-methylhydantoin (EMH) into the water, eventually leading to the buildup of high concentrations of DMH or EMH in the water. High concentrations of DMH or EMH inhibit the biocidal activity of the hypobromous acid by virtue of the following equilibria:



where BDMH is bromo-DMH and BEMH is bromo-EMH. This effect has previously been noted in U.S. Pat. No. 4,698,165.

As an alternative to the hydantoins, hypobromous acid may be prepared by reacting a bromide salt with a source of hypochlorite species according to the following equation:



as previously taught, for example, in British Patent 1,327,

531 and U.S. Pat. Nos. 2,815,311; 3,975,271; and 4,119,535. The hypobromous acid formed by the above equation is the active biocide. However, in the process of killing microorganisms or oxidizing organic material, the hypobromous acid is reduced to form bromide ion, as shown by the following equation:



Thus, the bromide ion can be reused to generate more hypobromous acid by reaction with hypochlorite species as shown above in equations 6a and 6b. Because the bromide ion is continuously reused, only small amounts of bromide ion are necessary to make a chlorine-based biocide in combination with bromide salts perform as a bromine biocide.

Some prior art teaches that, when using mixtures of chlorine-based biocides in combination with bromide salts, large excesses of bromide ion should be maintained in the recirculating water. For example, British Patent No. 1,327, 531 describes a process for sanitizing swimming pool water wherein the concentration of bromide is maintained at 20 to 50 mg per liter (expressed as sodium bromide) and the concentration of the hypobromite species is maintained at 0.4 mg/L. Other prior art, e.g., U.S. Pat. No. 3,975,271, suggests that when hypobromous acid is generated by reacting a bromide salt with a source of hypochlorous acid, the optimum mole ratio of chlorine to bromide is near 1. However, no information is provided as to how to maintain the ratio near the optimum in the recirculating water while chlorine and bromide salts are being fed simultaneously to the system as well as being lost from the system.

## SUMMARY OF THE INVENTION

This invention is broadly concerned with compositions and methods for controlling biofouling and microorganism population levels in recirculating water systems using compositions or combinations of hypochlorite donors and bromide ion donors.

The proportion of hypochlorite donor and bromide ion donor in the composition or combination added to the system is selected to maintain an optimum ratio of all bromine containing species to the sum of all hypohalite species in the recirculating water. It has now been found that significant amounts of bromide ion are lost from recirculating water systems through the pathways of volatilization of hypobromous acid and bromamines and of formation of stable organobromine compounds. Moreover, hypochlorite species, hypobromite species, and bromide ion are lost from the recirculating water at different rates. These loss rates must be known in order to prescribe at what rates to feed the hypochlorite donor and bromide ion donor to the water to compensate for the losses and maintain the desired steady state concentrations.

It is very important, therefore, to control the chemistries of the reactions of the hypochlorite species with the bromide ion (equations 6a and 6b) in a dynamic system. More specifically, it is critical to control the mole ratio of the sum of all bromine-containing species ( $\text{HOBr}$ ,  $\text{OBr}^-$  and  $\text{Br}^-$ ) to the sum of all hypohalite species ( $\text{HOBr}$ ,  $\text{OBr}^-$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ ) present in the water. For the purposes of this discussion, this mole ratio will be referred to herein as the "chlorine-to-bromine conversion ratio" or "Conversion Ratio" ("CR") and will be written as:

$$CR = \frac{\text{moles of (HOBr + OBr}^- + \text{Br}^-)}{\text{moles of (HOBr + OBr}^- + \text{HOCl + OCl}^-)}$$

This ratio will be used hereafter because it is a convenient way to express the instantaneous measure of the extent of conversion of the hypochlorite species to hypobromite species. It is also a convenient way to establish if the hypochlorite donor/bromide ion donor compositions are actually performing as a bromine biocide, a mixture of bromine and chlorine biocides, or as a chlorine biocide only. For example, consider the following four scenarios.

In the first scenario, the recirculating water does not contain any bromide ion. It follows then that there will be no hypobromite species present. Since the  $[\text{Br}^-] = 0.0$  and the  $[\text{HOBr}] = [\text{OBr}^-] = 0.0$ , then hypochlorite species will have some finite values; e.g., 0.5 mole of HOCl and 0.5 mole of  $\text{OCl}^-$ . Also,  $CR = 0.0$  as shown by the following calculation:

$$CR = \frac{(0.0 + 0.0 + 0.0)}{(0.0 + 0.0 + 0.5 + 0.5)} = \frac{0.0}{1.0} = 0.0$$

Under these conditions, the biocide will perform as a chlorine biocide.

Assume in the second scenario that the recirculating water contains 0.5 mole of bromide ion, 0.5 mole of HOCl and 0.5 mole of  $\text{OCl}^-$  before the hypochlorite species/bromide ion reactions occur. Under these conditions, there is only enough bromide ion to satisfy one-half of the stoichiometric requirements of the reactions outlined in equations 6a and 6b. Therefore, essentially all of the bromide ions will be converted to hypobromite species, but only one-half the hypochlorite species will be converted to hypobromite species. Also, one-half the hypochlorite species will still be present. Thus, the hypochlorite species in the water will be a 50/50 mixture of hypochlorite species and hypobromite species and the CR will be 0.5 as shown by the following calculation:

$$[\text{HOBr}] + [\text{OBr}^-] = 0.5 \text{ mole}$$

$$[\text{HOCl}] + [\text{OCl}^-] = 0.5 \text{ mole}$$

$$[\text{Br}^-] = 0.0$$

$$CR = \frac{(0.5 + 0.0)}{(0.5 + 0.5)} = \frac{0.5}{1.0} = 0.5$$

Since the hypochlorite donor/bromide ion donor composition is capable of only maintaining a 0.5 Conversion Ratio, it will exhibit biocidal properties intermediate between that of a chlorine biocide and a bromine biocide. It follows then that any hypochlorite donor/bromide ion donor composition that maintains a Conversion Ratio between 0.0 and 1.0, will exhibit the same properties.

In the third scenario, assume that there are 1.0 mole of bromide ion and 1.0 mole of hypochlorite species (0.5 mole of HOCl and 0.5 mole  $\text{OCl}^-$ ) before the  $\text{HOCl/Br}^-$  and  $\text{OCl}^-/\text{Br}^-$  reactions occur. Under these circumstances, essentially all of the hypochlorite species will be converted to hypobromite species. Similarly, essentially all of the bromide ions will be converted to hypobromite species. Hence, there will be essentially no hypochlorite species and bromide ions left. As a consequence, after the reactions, the Conversion Ratio will be 1.0 as shown by the following calculation:

$$[\text{Br}^-] = 0.0$$

$$[\text{HOCl}] = [\text{OCl}^-] = 0.0$$

$$[\text{HOBr}] + [\text{OBr}^-] = 1.0$$

$$CR = \frac{(1.0 + 0.0)}{(0.0 + 1.0)} = \frac{1.0}{1.0} = 1.0$$

And, the hypochlorite donor/bromide ion donor composition will perform as a bromine biocide.

Finally, in the fourth scenario, assume that the recirculating water contains 1.2 moles of bromide ion and 1.0 mole of hypochlorite species before the hypochlorite species react with the bromide ion. Upon completion of these instantaneous reactions, the recirculating water will contain essentially no hypochlorite species, 1.0 mole of hypobromite species and 0.2 mole of bromide ion. Accordingly, after the reactions, the Conversion Ratio will be 1.2 as shown below:

$$[\text{HOCl}] = [\text{OCl}^-] = 0.0$$

$$[\text{HOBr}] + [\text{OBr}^-] = 1.0$$

$$[\text{Br}^-] = 0.2$$

Thus,

$$CR = \frac{(1.0 + 0.2)}{(1.0 + 0.0)} = \frac{1.2}{1.0} = 1.2$$

As a consequence, the hypochlorite donor/bromide ion donor composition will perform as a bromine biocide.

Thus, it is desirable to maintain the Conversion Ratio preferably at or slightly above 1.0. However, as will be shown later, there are circumstances where other Conversion Ratios are desirable. Hence, it is preferable to maintain the Conversion Ratio between about 0.2 and 20.0 and most preferably between 0.5 and 4.0.

In order to control the Conversion Ratio to maintain a small excess of bromide ion, enough bromide ion must be fed to the water to compensate for any significant losses of bromine containing species. Bromide ion is, of course, lost from recirculating water systems through blowdown or turnover. These terms refer to water that is bled from the system, a practice necessary to keep dissolved solids from building up to the point where scaling occurs. However, there has been no recognition in the literature that bromide ion is lost by volatilization of hypobromous acid and bromamines when combinations of hypochlorite donors and bromide ion donors are used to generate hypobromite species. Moreover, the literature contains no recognition that significant bromide ion losses can occur through the reaction of hypobromite species with organic materials in the recirculating water. Nor has the literature recognized the magnitude and the rate of bromide ion losses that can result from the volatilization and organobromine compound pathways. More importantly, the literature contains no recognition that knowledge of the bromide ion loss phenomenon may be used to develop compositions comprising hypochlorite donors and bromide ion donors that are capable of simultaneously compensating for the bromide ion losses and satisfying the chlorine demand of the recirculating water. Without knowledge of bromide ion loss pathways, as will be shown in the detailed description of this invention, it is virtually impossible to develop commercial products that will perform like bromine-based biocides without using a

large excess of bromide ion. Thus, all significant pathways of bromide ion loss must be accounted for in order to maintain an optimum Conversion Ratio in the recirculating water.

The failure of the prior art to adequately compensate for bromide ion loss is evident in the prior art's use of either large excesses of bromide ion or of insufficient amounts to maintain maximum biocidal activity. Any large excess of bromide ion is wasted since it is eventually discarded, for example, in the cooling tower blowdown or pool water turnover. Also, as will be shown in the detailed description of the present invention, a large excess of bromide ion is unnecessary because the physical and chemical dynamics of the recirculating water system will force the bromide ion concentration to a steady state condition. In many cases, this will result in considerable loss of bromide ion. As a consequence, it is preferable and more economical to supply only sufficient bromide ion to the recirculating water to maintain the Conversion Ratio at, or slightly above, 1.0 to ensure maximum biocidal effectiveness.

In one aspect, the present invention provides a biocide composition containing a hypochlorite donor and a bromide ion donor in amounts sufficient to satisfy the chlorine demand of the system and maintain an optimum Conversion Ratio.

In another aspect, the present invention provides a method of treating recirculating water which comprises the steps of ascertaining the rates of bromide ion loss from the system due to blowdown, volatilization, and formation of stable organobromine compounds and adding a hypochlorite donor and a bromide ion donor in amounts sufficient to compensate for the bromide ion losses and maintain an optimum Conversion Ratio.

Suitable hypochlorite donors include gaseous chlorine, alkali metal and alkaline earth metal hypochlorites, chlorinated hydantoins, chlorinated oxazolidinones, chlorinated imidazolidinones, and chlorinated isocyanuric acid derivatives.

Suitable bromide ion donors include liquid bromine, bromine chloride, alkali metal and alkaline earth metal bromides, quaternary ammonium bromides, bromamines, brominated hydantoins, brominated sulfonamides, brominated succinimides, brominated oxazolidinones, brominated imidazolidinones, brominated isocyanurates, and salts of trihalide or mixed trihalide ions containing bromine.

In a preferred embodiment the hypochlorite donor and bromide ion donor are dry solids having a higher dissolution rate and a higher water solubility than hydantoins. Preferred dry solids include trichloroisocyanuric acid or sodium or potassium dichloroisocyanurate and sodium or potassium bromide. When these compounds are used, it has been found that proportions of about 85 to about 99 parts by weight hypochlorite donor and about 1 to about 15 parts by weight bromide ion donor are capable of maintaining the Conversion Ratio in the optimum range for most water systems. In other instances, e.g. when hydantoin derivatives are used as the bromide ion donor, different proportions are sometimes necessary. For these compounds, it has been found that proportions of about 50 to about 99 parts by weight hypochlorite donor and about 1 to about 50 parts by weight bromide ion donor are capable of maintaining an optimum Conversion Ratio.

It has now also been found that certain compounds can be added to the recirculating water system to suppress the loss of bromide ions through volatilization of hypobromous acid and bromamine. The bromine volatilization suppressants may be included in the hypochlorite donor/bromide ion donor biocide composition or combination thereof or may be

added separately to the recirculating water. Suitable bromine volatilization suppressants include hydantoin derivatives, sulfonamide derivatives, sulfamic acid derivatives, glycoluril derivatives, oxazolidinone derivatives, imidazolidinone derivatives and succinimide derivatives.

Other features and advantages of the present invention will become apparent from the following detailed description, which is given by way of illustration only.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the effect of the Conversion Ratio on killing efficiency.

FIGS. 2-6 illustrate the effect of the hypochlorite donor/bromide ion donor composition on the Conversion Ratio in the recirculating water and the ability of the biocide to perform as a bromine biocide. NaBr/ACL90 PLUS and NaBr/ACL60 compositions are used to illustrate the effects.

FIG. 7 illustrates the effect of DMH on the Henry's Law constant for a bromine biocide.

## DETAILED DESCRIPTION OF THE INVENTION

A hypochlorite donor compound according to the present invention may be any chlorine containing compound capable of providing a sufficient amount of hypochlorite species in aqueous solution, including but not limited to gaseous chlorine, hypochlorite salts such as lithium hypochlorite, sodium hypochlorite, or calcium hypochlorite, chlorinated hydantoins such as dichlorodimethylhydantoin, or bromochlorodimethylhydantoin, chlorinated oxazolidinones such as 3-chloro-4,4-dimethyl-2-oxazolidinone, chlorinated imidazolidinones such as 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, or chlorinated isocyanuric acid or its derivatives including its salts, hydrates, complexes, or mixtures thereof.

Some disadvantages may occur with the use of certain of these hypochlorite donor compounds. For example, addition of calcium is not desirable since repeated use could increase the calcium ion concentration in the water to the level where calcium scaling problems could occur. Since chlorine gas is a hazardous material, its use is generally limited to the larger, more sophisticated recirculating water systems. Finally, many of the chlorinated organic compounds are less useful than the chlorinated isocyanuric acid derivatives due to higher costs, lower dissolution rates, lower halogen content, and/or the buildup of species which inhibit biocidal activity.

Preferred hypochlorite donor compounds include chlorinated isocyanuric acid derivatives chosen from the following group of compounds: sodium dichloro-s-triazinetriene (also called sodium dichloroisocyanurate, available from Monsanto Co. under the tradename ACL60), potassium dichloro-s-triazinetriene (available from Monsanto Co. under the tradename ACL59), the hydrate of sodium dichloro-s-triazinetriene (available from Monsanto Co. under the tradename ACL56), dichloroisocyanuric acid, trichloro-s-triazinetriene (also called trichloroisocyanuric acid, available from Monsanto under the tradename ACL90 PLUS), mixtures thereof such as [mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene and [mono(trichloro)-mono(monopotassiumdichloro)]-di-s-triazinetriene. These compounds are disclosed, for example, in U.S. Pat. Nos. 3,035,056; 3,035,057; 3,150,132; 3,256,199; 3,294,797; and 3,564,146.

The bromide ion donor according to the present invention may be any compound capable of providing a sufficient amount of bromide ion in aqueous solution including, but not limited to, liquid bromine, bromine chloride, alkali metal bromides, alkaline earth metal bromides,  $R_4$ -ammonium bromide where R is an alkyl or aryl group, bromamines, N-brominated organic compounds, such as N-brominated hydantoins, N-brominated sulfonamides, N-brominated oxazolidinones, N-brominated imidazolidinones; N-brominated imides such as N-bromosuccinimide or N-brominated isocyanurates which can release hypobromite species or salts of trihalide or mixed trihalide ions such as  $Br_3^-$  or  $ClBr_2^-$  as described in U.S. Pat. No. 3,152,073.

The hypochlorite donor compound and the bromide ion donor compound may be added either separately or as a single composition. For some combinations, the two components must be added separately, for example, chlorine gas and sodium bromide. In many cases, however, it is advantageous to premix the two components and add the compositions to the recirculating water system. This reduces the number of materials to be handled and thus the number of controls required. Thus, it is possible to introduce the biocide of the present invention into the recirculating water system by any of the following means: an erosion feeder, a floater, porous bags, perforated buckets or by hand dosing.

A preferred product is a solid dry mixture of a chlorinated isocyanuric acid derivative and a bromide ion donor, most preferably compacted in the form of a tablet, stick or puck. One or more compacting aids such as boric acid, sodium stearate, potassium stearate, aluminum hydroxide or monoglycerol stearate may optionally be used. To eliminate any possible interaction between the two components of the mixture it is necessary to eliminate any free water, as taught in U.S. Pat. No. 2,815,311. If free water is present, the two components may react to form bromine gas, which can corrode metallic containers or pose a health hazard to persons handling the material. In addition to optional compacting aids, the biocide of the present invention may also optionally include one or more scale inhibitor compounds such as polymaleic acid, polyacrylic acid, a phosphonate, a polyphosphate, or mixtures thereof.

When the product used is a mixture of a solid hypochlorite donor and a bromide ion donor, the appropriate composition depends on the operating characteristics of the individual recirculating water system. Therefore a range of compositions is required since there are a number of differences between systems. These differences include variation in the quality of the water used for makeup, variation in local air quality, variation in the blowdown or turnover rate, and other system variables. For a composition of trichloroisocyanuric acid and sodium bromide, the weight percent of sodium bromide in the composition required to provide the optimum Conversion Ratio in the recirculating water typically ranges from about 3% NaBr to about 15% NaBr, depending on how the recirculating water system is operated.

To maintain the Conversion Ratio in solution at the desired optimum, it is necessary to control both the sum of the concentrations of the hypohalite species ( $HOCl$ ,  $OCl^-$ ,  $HOBr$ , and  $OBr^-$ ) and the sum of the concentrations of all bromine containing species ( $HOBr$ ,  $OBr^-$ , and  $Br^-$ ).

Control of the free halogen concentration is straightforward and is normally achieved for most systems, either with automated analyzer/control equipment or manually with the use of analytical test kits. Test kits and analytical control equipment determine free halogen concentrations by measuring the oxidizing potential of the species dissolved in the

water. However, these devices are incapable of distinguishing whether the oxidizing potential was due to hypochlorite or hypobromite species. Consequently, the free halogen concentrations measured in the recirculating water systems are the sum of the free chlorine and the free bromine, and will usually be expressed in terms of free chlorine, since chlorine test kits are more widely used. The free halogen concentrations may also be expressed in terms of free bromine by: (1) multiplying the free chlorine reading by 2.25, which is the ratio of the molecular weights of molecular bromine to molecular chlorine ( $160/71=2.25$ ) or (2) using a bromine test kit. However, when the Conversion Ratio in the recirculating water is one or greater, all of the free halogen species will be present as free bromine species, even though the free bromine may be expressed in terms of free chlorine.

Initially, it was believed that bromide ion would be a conserved specie in recirculating water systems, that is, that blowdown or turnover would be the only significant pathway for bromide ion loss. Blowdown or turnover loss,  $BrL(BD)$ , may be calculated using the following equation, assuming constant bromide ion concentration:

$$BrL(BD) = Q_b \times C_{Br} + \frac{3.79}{1000} \quad (9)$$

where:

$BrL(BD)$  = bromide ion loss due to blowdown, gm/day

$Q_b$  = blowdown or turnover rate, gal/day

$C_{Br}$  = total concentration of all bromine species, mg/liter

3.79 = conversion factor, gallons to liters

1000 = conversion factor, grams to milligrams

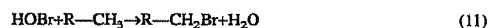
Example: a system contains 1.0 mg Br/liter distributed between bromide ion and hypobromite species, and has a blowdown rate of 1000 gal/day. The calculated bromide ion loss due to blowdown would then be 3.79 gm Br/day.

Measurement of the bromide ion concentration during initial experiments has unexpectedly revealed the existence of other significant pathways of bromide ion loss. Further investigation has now demonstrated that in order to maintain an optimum Conversion Ratio, it is necessary to compensate for bromide ion losses by three additional pathways: 1) volatilization of hypobromous acid, 2) volatilization of bromamines and 3) formation of organobromine compounds. Loss of bromide ion by the volatilization of hypobromous acid occurs as a result of the reaction described in equation (6a).

Bromide ion losses via volatilization of bromamines occurs as a consequence of the reaction between hypobromous acid and nitrogenous contaminants (expressed in terms of ammonia).



Organobromine compound formation occurs due to the reaction of hypobromous acid with organic matter in the water to form compounds with carbon-bromine bonds, for example:



The organobromine compounds include the trihalomethanes or other brominated alkanes, brominated carboxylic acids, and the like. The carbon-bromine bonds are very stable and not readily hydrolyzed. Hence, the bromine specie is no longer available as bromide ion for regeneration to hypobromous acid by hypochlorous acid. Therefore, the bromide

13

ion has been effectively removed from this chemical recycle loop.

It is necessary to establish the magnitude of the bromide ion losses by these pathways in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. This can be accomplished by two methods: 1) analytical determination of the decrease in bromide ion concentration ("the bromide ion analytical method") and 2) calculation of losses by the different pathways.

The determination of the appropriate amounts of bromide ion donor and hypochlorite donor can be achieved by the bromide ion analytical method as outlined in the following:

1. Take samples of the recirculating water at regular intervals and note the sample times.

2. Determine the bromide ion concentration of the water samples with ASTM D-1246-82a, Method D-Ion Selective Electrode For Bromide. Note, in this case, the hypohalite species (HOBr, OBr<sup>-</sup>, HOCl, OCl<sup>-</sup>) must be converted to halide species (Cl<sup>-</sup> and Br<sup>-</sup>) prior to the determination of bromide ion. This is achieved by adding sodium sulfite to the solutions in amounts of 1.25 times the stoichiometric amount required to satisfy the following equation:



where:

OX<sup>-</sup>=OCl<sup>-</sup> or OBr<sup>-</sup>

X<sup>-</sup>=Cl<sup>-</sup> or Br<sup>-</sup>

3. Calculate the total daily loss of bromide ion TBrL, in grams per day by using the analytical and sample time data.
4. Determine the amount of bromide ion donor, BrD, required to compensate for the losses and maintain the bromide ion concentration at the desired level with the following equation:

$$\text{BrD} = \frac{M_{\text{BrD}}}{M_{\text{Br}}} \times \text{TBrL} \quad (13)$$

where:

BrD=amount of bromide ion donor required to compensate for losses and maintain the bromide ion concentration at the desired level, gm/day

M<sub>BrD</sub>=mole weight of bromide ion donor, gm

M<sub>Br</sub>=mole weight of bromide ion, gm

TBrL=total daily bromide ion losses, gm/day

5. Determine the daily chlorine demand, CD, of the system.
6. Determine the amount of hypochlorite donor compound required to satisfy the daily chlorine demand with the following equation:

$$\text{HCD} = \frac{\text{CD}}{\text{AvC}} \times 100\% \quad (14)$$

where:

HCD=amount of hypochlorite donor compound required to satisfy the chlorine demand, gm/day

CD=chlorine demand of the system, gm Cl<sub>2</sub>/day

AvC=available chlorine content of chlorine donor (wt %)

14

7. For hypochlorite donor/bromide ion donor combinations where it is more practical to feed the two donors separately, the results of steps 4 and 6 indicate what the feed rates must be for the corresponding donors in order to satisfy the chlorine demand and bromide ion donor requirements and to make the combinations perform as bromine biocides.

8. For a hypochlorite donor/bromide ion donor combination that will be contained in a single composition or product, a composition is determined by the following calculations:

- a. Hypochlorite Donor/Bromide Ion Donor Composition Requirements

$$\text{BGC} = \text{HCD} + \text{BrD} \quad (15)$$

where:

BGC=amount of hypochlorite donor/bromide ion donor composition required to satisfy the chlorine demand and bromide ion requirements simultaneously, gm/day

- b. Hypochlorite Donor/Bromide Ion Donor Composition.

$$\% \text{ hypochlorite donor} = \frac{\text{HCD}}{\text{BGC}} \times 100\% \quad (16)$$

$$\% \text{ bromide ion donor} = \frac{\text{BrD}}{\text{BGC}} \times 100\% \quad (17)$$

Although it is an alternative to calculating the appropriate amounts of bromide ion donor and hypochlorite donor to feed to the system, the bromide ion analytical approach is generally beyond the sophistication of most cooling tower, swimming pool and spa operations or would require a considerable expense for added instrumentation.

The present invention obviates the need for this costly instrumentation, since the appropriate amounts of hypochlorite donor and bromide ion donor may also be established by the second method, that is, by calculating bromide ion losses. Investigations relating to the present invention demonstrate that the bromide ion can be lost by pathways other than blowdown. At the optimum Conversion Ratio, the losses incurred by these pathways can be several times larger than the blowdown loss, making it virtually impossible to maintain the desired Conversion Ratio without knowledge of these pathways. The magnitudes of the losses by the various pathways are totally surprising. At Conversion Ratios much higher than optimum, the percentage of the total bromide ion lost by these pathways is much lower, because the ionic bromide form is not volatile. In such cases, the volatilization losses are not readily apparent. Thus, since prior art use of bromide-based biocides was not at the optimum Conversion Ratio, the loss of bromide ion by these pathways was not recognized. Because bromide ion was usually present in excess, the prior art did not perceive the importance of these additional bromide ion loss pathways.

The amount of bromide ion lost by flashoff of HOBr, BrL(FL), may be calculated using either equation (18) or (19).

$$\text{BrL(FL)} = \frac{f \times H_k}{W_f/W_G} \times R \times C_{\text{HOBr}} \times \frac{M_w}{M_a} \times \frac{M_{\text{Br}}}{M_{\text{HOBr}}} \times \frac{3.79}{1000} \quad (18)$$

or

-continued

$$\text{BrL(FL)} = f H_k Q_a D_a C_{\text{HOBr}} \times \frac{M_w}{M_a} \times \frac{M_{\text{Br}}}{M_{\text{HOBr}}} \times \frac{28.316}{1000} \times 1440 \quad (19)$$

where:

BrL(FL)=amount of bromide ion lost by flashoff hypobromous acid, gm Br/day

R=the recirculation rate of the recirculating water system, gal/day

f=flashoff equilibrium coefficient for the recirculating water system. (Note, f has a value between 0 and 1.)

 $H_k$ =Henry's Law Constant for hypobromous acid at the pH and temperature of the recirculating water system

Q=the flow rate of air through the tower, ft/min.

 $D_a$ =density of air, gm/L $W_L/W_G$ =ratio of the mass flow rate of the recirculating water to the mass flow rate of air through the system $M_{\text{HOBr}}$ =mole weight of hypobromous acid, gm $C_{\text{HOBr}}$ =the concentration of hypobromite species as hypobromous acid, mg HOBr/L $M_w$ =mole weight of water, gm $M_a$ =mole weight of air, gm $M_{\text{Br}}$ =mole weight of bromide ion, gm

3.79=conversion factor, gallons to liters

1000=conversion factor, grams to milligrams

28.316=conversion factor, cubic feet to liters

1440=conversion factor, days to minutes

It is important to point out that the value of  $C_{\text{HOBr}}$ , the concentration of hypobromite species, is not the same as  $C_{\text{Br}}$ , the sum of concentrations of all bromine-containing species, since some of the bromine species present can be in the form of bromide ion.

Henry's Law constant is defined by the following equation:

$$H_k = \frac{C_{\text{solute (gas)}}}{C_{\text{solute (liquid)}}} \quad (20)$$

where:

 $H_k$ =Henry's Law Constant $C_{\text{solute (gas)}}$ =concentration of volatile solute in the gas phase $C_{\text{solute (liquid)}}$ =concentration of volatile solute in the liquid phase

Henry's Law constant is, therefore, the ratio of the concentration of solute in the vapor phase at equilibrium to the concentration of the solute dissolved in a solvent, in these cases water. This constant is a measure of the tendency of the dissolved solute to escape or volatilize from the solvent. A low Henry's Law constant indicates little tendency for the solute to volatilize. A high constant value indicates a greater tendency of the solute to escape from the solution into the gas phase. Henry's Law constants can be expressed in any combination of a number of concentration units, such as partial pressure, milligrams per liter, or mole fraction. Herein, mole fraction units are used for both the gas and liquid phase concentrations.

As an example, a cooling tower has  $W_L/W_G=1.3$ ,  $f=0.5$ ,  $R=400,000$  gallons/day, and the tower operates at pH=8.0 and 30° C. For the conditions in this particular example, Henry's Law constant is 0.25. The concentration of free halogen is 0.5 mg/L (0.5 ppm, free chlorine basis). The bromide ion concentration is maintained at 0.8 mg/L (0.8

ppm) to give a Conversion Ratio of 1.05, slightly greater than the optimum value of 1. Thus, all of the free halogen species are essentially free bromine species (HOBr and OBr<sup>-</sup>). As a result, the free bromine concentration in terms of hypobromous acid is 0.685 mg/L [ $C_{\text{HOBr}} = \text{FAV} \times M_{\text{HOBr}} / M_{\text{Cl}_2} = 0.5 \times 96.9 / 71 = 0.685$ ]. Under these conditions, the flashoff loss of bromide ion via the volatilization of hypobromous acid is 51.1 grams of bromide ion per day. This loss is considerably larger than that due to blowdown (cf. blowdown loss calculation above), demonstrating that volatilization of hypobromous acid can be a major factor contributing to the loss of bromide ion from recirculating water systems.

The Henry's Law constant for hypobromous acid used in the above example was determined as follows, using a pilot scale cooling tower since there is no literature data for hypobromous acid or any of the bromamines. The pilot cooling tower was a counterflow type with a capacity of 80 liters of water, which was circulated through the tower at 1.2 gal/min. The air flow rate was 2800 L/min. An electrical heater, placed in the recirculation line, provided a constant heat source. In each experiment, the pilot tower was filled with chlorine-demand-free water and an appropriate amount of biocide was added to give 4.0 mg/L (as chlorine). During the test, the biocide concentration was continuously monitored using a Hach CL17 chlorine analyzer. The water was initially recirculated with no air flow for 30 minutes to establish a baseline free halogen concentration. The air flow was then started and the free halogen concentration was monitored for four hours. The drop in the halogen concentration during this period, which is due to volatilization of any volatile species, can be used to calculate the Henry's Law constant using the following equation:

$$H = - \frac{(\log C_f - \log C_i)}{t} \times \frac{2.303 V_w D_w M_a}{Q_a D_a M_w}$$

where:

 $H_k$ =Henry's Law constant at temperature and pH of the experiment $V_w$ =volume of recirculating water, liters $D_w$ =density of water, gm/ml $D_a$ =density of air, gm/ml $M_w$ =mole weight of water, gm $M_a$ =mole weight of air, gm $Q_a$ =volumetric air flow, L/min $C_f$ =final halogen concentration, mg/L $C_i$ =initial halogen concentration, mg/L $t$ =length of time of experiment, min

This procedure assumes that the hypobromous acid has reached equilibrium between the gas and liquid phases. With this method, Henry's Law constants were determined for hypobromous acid as a function of pH, temperature, and the concentration of additional chemical species.

As stated previously, the presence of ammonia in the recirculating water has also been found to increase the loss of bromide ion. This is due to the formation of various bromamine compounds, especially monobromamine, which is more volatile than hypobromous acid. The effect of ammonia on the volatility of hypobromous acid is reflected in an increase in the Henry's Law constant. This change in the Henry's Law constant is dependent on the ratio of ammonia to free bromine, the pH, and the temperature. There are no literature values for the Henry's Law constants for bromamines. The results of our measurements indicate the Henry's Law constant for bromamines is considerably

17

larger than the Henry's Law constant for hypobromous acid under the same conditions. The simple bromamines are, therefore, very volatile and do not build up to significant levels because they are flashed off very rapidly.

Under steady state conditions, the loss of the simple bromamines by flashoff will be approximately equal to the rate of formation of monobromamine. The bromamine formation rate is determined by the rate of introduction of ammonia into the recirculating water. In most cases, the major source of ammonia is the makeup water. Thus, the flashoff loss due to formation of bromamines, BrL(BA), can simply be estimated by the following equation:

$$\text{BrL(BA)} = C_{\text{NH}_3} \times Q_m \times \frac{M_{\text{Br}}}{M_{\text{NH}_3}} \times \frac{3.79}{1000} \quad (21)$$

where:

BrL(BA)=amount of bromide ion lost by flashoff of bromamines, gm/day

$C_{\text{NH}_3}$ =concentration of ammonia in makeup water, mg/L

$Q_m$ =makeup water rate, gal/day

$M_{\text{Br}}$ =mole weight of bromide ion, gm

$M_{\text{NH}_3}$ =mole weight of ammonia, gm

3.79=conversion factor, gallons to liters

1000=conversion factor, grams to milligrams

Note, equation (21) applies only to relatively small ammonia concentrations.

Another significant pathway for bromide ion loss is the formation of organobromine compounds as a result of the reaction of hypobromous acid with organic molecules dissolved or suspended in the water. Carbon-bromine covalent bonds are usually stable to hydrolysis so that the bromine is not released back into the water and is not available for regeneration to hypobromite species. The amount of bromide ion loss can vary widely depending on the organic content of the water, which can be quantified as TOC. TOC, or total organic carbon (in mg/L), measures the total amount of organic material dissolved or suspended in the water, without distinguishing the chemical form. Several commercial analyzers are available which perform this analysis. Lab experiments with both tap water and untreated surface water have shown that about 0.2 mg/L of bromide ion is combined as organobromine compounds for every mg/L of TOC introduced into the water. This number varies somewhat depending on the individual water source, but 0.2 is a reasonable estimate for most cases.

The amount of bromide ion loss caused by the formation of organobromine compounds, BrL(OBr) can be calculated with the following equation, which accounts for the total organic carbon introduced with the makeup water:

$$\text{BrL(OBr)} = Q_m \times 0.2 \times \text{TOC} \times \frac{3.79}{1000} \quad (22)$$

where:

BrL(OBr)=amount of bromide ion lost due to the formation of organobromine compounds, gm/day

$Q_m$ =makeup water rate, gal/day

TOC=total organic content of makeup water, mg/L

0.2=amount of bromide ion lost per mg/L of TOC in recirculating water, mg/L

3.79=conversion factor, gallons to liters

1000=conversion factor, grams to milligrams

Note, equation (22) applies only to relatively small TOC concentrations. This calculation does not account for any

18

TOC added from sources other than makeup, for instance, organic or biological contamination absorbed from the air blown through the tower or contamination from process leaks. If such contamination is severe, the additional loss of bromide ion by reaction with these sources of TOC should also be accounted for.

It is necessary to quantify the major pathways of bromide ion loss, blowdown, flashoff, and organobromine formation in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. Once each of the bromide ion pathway losses are quantified, the optimum proportions of bromide ion donor and hypochlorite donor to be fed to the system may be calculated according to the following steps:

- 1) Define the desired free halogen concentration (available chlorine basis), FAVC, and the desired Conversion Ratio, CR. CR may range from about 0.2 to about 20.0, more preferably from about 0.2 to about 10.0, and most preferably from about 0.5 to about 4.0. If excess bromide ion is desired CR should be greater than 1.0; if not, then CR can be less than 1.0.
- 2) Convert the desired free halogen concentration to the concentration of hypobromous acid,  $C_{\text{HOBrr}}$ , by multiplying the free chlorine concentration, FAVC, by 1.37×RCR if CR is less than 1.0 or by 1.37 if CR is greater than 1.0. The factor 1.37 is equal to 96,916/70,906 (molecular weight of HOBr/molecular weight of chlorine).
- 3) Calculate the desired total concentration of all bromine containing species,  $C_{\text{Br}}$ , in terms of bromide ion, using the following equation:

$$C_{\text{Br}} = \text{FAVC} \times \text{CR} \times \frac{M_{\text{Br}}}{M_{\text{Cl}_2}}$$

- 4) Calculate the daily bromide ion loss caused by blowdown, BrL(BD), with equation (9).
- 5) Calculate the daily bromide ion loss incurred by the flashoff of hypobromous acid, BrL(FL), using either equation (18) or (19).
- 6) Calculate the daily bromide ion loss caused by bromamine flashoff, BrL(BA), with equation (21).
- 7) Calculate the daily bromide ion loss caused by the formation of organobromine compounds, BrL(OBr), using equation (22).
- 8) Calculate the total daily bromide ion loss, TBrL, by combining the results of the calculations in steps 4, 5, 6, and 7.

$$\text{TBrL} = \text{BrL(BD)} + \text{BrL(FL)} + \text{BrL(BA)} + \text{BrL(OBr)} \quad (23)$$

- 9) Determine the daily quantity of bromide ion donor required to compensate for bromide ion losses with equation (13).
- 10) Determine the amount of hypochlorite donor required to satisfy the daily chlorine demand with equation (14).
- 11) For hypochlorite donor/bromide ion donor combinations where it is more practical to feed the two donors separately, the results of steps 9 and 10 indicate what the feed rates must be for the corresponding donors in order to satisfy the chlorine demand and bromide donor requirements simultaneously and make the combination perform as a bromine biocide.
- 12) For products containing both the hypochlorite donor and bromide ion donor as a single composition or mixture, determine the appropriate composition with equations (15), (16) and (17).



The effectiveness of the hypochlorite donor/bromide ion donor biocides and the bromine volatilization suppressants disclosed herein is demonstrated in the following examples, including killing efficiency experiments, cooling tower and spa tests, and calculations in which compositions representative of the present invention, such as ACL60/NaBr and ACL90 PLUS/NaBr, are compared with chlorine (ACL60) and competitive bromine (BCDMH) biocides.

#### Example 1—Effectiveness of Hypochlorite Donor/Bromide Ion Donor Compositions In Cooling Towers

A small crossflow, induced draft cooling tower, used to cool a 250 ton air conditioning system, was used to test the relative effectiveness of the current invention versus chlorine and BCDMH biocides over a period of five months. The pH of the tower water was controlled at 8.5 and the free halogen concentration was controlled at 0.5 mg/L (available chlorine base) with an automated chlorine analyzer/controller. Scale and corrosion inhibitors were also added as part of the normal operation of the cooling tower. The effectiveness of each biocide was judged on the ability of the biocide to control the biofouling microorganism population as measured by a standard plate count method. Microorganism populations were reported as colony forming units per milliliter (CFU/ml). Samples for the determination of microorganism populations and bromide ion concentration were taken from the same location in the cooling tower basin away from the point of chemical addition. Two to three samples were taken per day. Immediately after sampling, any hypohalite species were reduced to halide species with sodium thiosulfate. The bromide ion concentration was measured by ion chromatography. The results of the test are shown below in Table 1:

TABLE 1

Results of Cooling Tower Biofouling Control Tests  
Comparing Biocidal Effectiveness of Hypochlorite  
Donor/Bromide Ion Donor Biocide Compositions to Chlorine  
and Bromine Biocides.

Biocide Tested	Total Br Conc (mg/L)	Plate Count (CFU/ml)	Conversion Ratio
ACL60	0.0	14,200	0.0
ACL60/NaBr	0.14	5,600	0.25
ACL90 PLUS/NaBr	1.8	4,200	3.2
BCDMH	23.2	24,600	41.1
ACL60/NaBr	18	1,600	31.9
ACL90 PLUS/NaBr	6.5	1,200	11.5

Notes:

- Results are the average values observed during the test periods.
- Test Conditions: pH = 8.5; free halogen = 0.5 mg/L, available chlorine basis.

In these tests, ACL60 (sodium dichloroisocyanurate) was used to demonstrate the biocidal effectiveness of chlorine biocides under these conditions. Combinations of sodium bromide with ACL60 and sodium bromide with ACL90 PLUS (trichloroisocyanurate) were employed to illustrate the effect of the Conversion Ratio on the biocidal effectiveness of the hypochlorite donor/bromide ion donor compositions, which are representative of the present invention, and their ability to perform as bromine biocides. BCDMH was also included to compare the effectiveness of this bromine biocide to the ones representative of the present invention.

The results of these tests show that the hypochlorite donor/bromide ion donor compositions of NaBr/ACL60 and ACL90 PLUS/NaBr, were not only superior to the chlorine biocide, ACL60, but were also superior to the bromine biocide, BCDMH, in controlling the population of the biofouling microorganisms. The most effective NaBr/ACL60 and NaBr/ACL90 PLUS biocide compositions were those which maintained the Conversion Ratio in the recirculating water above 1.

The biocide compositions that were less effective were those which produced Conversion Ratios of less than one. However, all of the NaBr/ACL compositions were more effective than the chlorine (ACL60) and BCDMH biocides, as evidenced by the fact that they controlled the biofouling microorganism population at or below 6000 CFU/ml, whereas the chlorine and BCDMH biocides were not capable of reducing the biofouling populations below 14,000 and 24,000 CFU/ml, respectively, at the same free halogen concentration.

#### Example 2

##### Effectiveness of Hypochlorite Donor/Bromide Ion Donor Biocide Compositions in Biofouling Control Experiments.

The killing efficiencies of the biocides evaluated in Example 1 were also determined in laboratory experiments designed to simulate cooling tower conditions. In these experiments, a culture of microorganisms from the cooling water in Example 1 were cultured in a well-stirred vessel by metering nutrient solution into the solution containing the culture. The vessel contents were maintained at 37° C. and pH of 8.0. Each experiment consisted of shocking the microorganisms with the biocide to be tested. Nutrient solution was also fed continuously to the vessel to encourage growth of the microorganisms and biocide solution was fed to the vessel to control the free halogen concentration at 0.5 mg/L (available chlorine basis) and the microorganism population. The microorganism population was determined periodically by an HMB-II apparatus (KVM Engineering) until the microorganism population had ceased to decline and remained constant for several hours. This usually occurred in about four hours after the start of the experiment. At this point, the microorganism growth rate and the microorganism death rate due to the biocidal activity of the biocide were considered to be in dynamic equilibrium, or at steady state. The effectiveness of biocide was then judged on the basis of killing efficiency as defined by the following expression.

$$KE = \frac{(P_i - P_f)}{P_i} \times 100\% \quad (24)$$

where:

KE=killing efficiency of the biocide, %

$P_i$ =microorganism population at the start of the experiment, CFU/ml

$P_f$ =microorganism population at steady state conditions, CFU/ml

The results of the biocide killing efficiency experiments are summarized in Table 2.

TABLE 2

Results of Biocide Killing Efficiency Experiments					
Biocide Tested	NaBr/AcL 60 Wt. Ratio	CR	P <sub>i</sub> (CFU/ml)	P <sub>f</sub> (CFU/ml)	KE
BCDMH	--	--	2,140,000	1,260,000	41
AGL60	0.0	0.0	1,560,000	880,000	44
ACL60/NaBr	0.1	0.13	1,960,000	830,000	58
ACL60/NaBr	0.19	0.22	1,410,000	350,000	75
ACL60/NaBr	1.0	1.20	1,460,000	165,000	89

Conditions: pH=8.5, temperature=37° C., free halogen=0.5 mg/L (available chlorine basis).

The results in Table 2 show that the NaBr/ACL60 compositions (hypobromous acid generating compositions) have superior biocidal activity relative to the chlorine biocide, ACL60, and the bromine biocide, BCDMH, under the conditions of the experiments. The results also support the validity of the results obtained in the cooling tower tests (Example 1). The above results also show that the best killing efficiency was obtained at a Conversion Ratio of 1.20. This represents the condition where the amount of NaBr is sufficient to make the bromide ion concentration in the water slightly in excess of the stoichiometric amount required to satisfy the reactions shown in equations (6a) and (6b). Thus, the best killing efficiency was obtained with the composition that performed as a true bromine biocide. However, the results of the experiments indicate that the killing efficiencies of NaBr/ACL60 compositions which yield Conversion Ratios of less than 1 are still better than the chlorine (ACL60) or BCDMH biocides.

The effect of the Conversion Ratio can be understood more clearly by referring to the graph shown in FIG. 1. FIG. 1 is a plot of the killing efficiency of each ACL60/NaBr composition tested as a function of the Conversion Ratio. The results show that killing efficiencies increase as the Conversion Ratios increase until the maximum killing efficiency is attained near a Conversion Ratio of 1.0. At this point, all of the free halogen species are free bromine species. FIG. 1 also shows that most of the improvement in killing efficiency (from 42% to 75%) occurred between Conversion Ratios of 0.0 and 0.2. This indicates that the Conversion Ratio in the recirculating water system does not have to be controlled tightly in order for the bromine based biocide to be significantly better than chlorine biocides at pH levels of 8 or higher.

Even though the performance of the hypochlorite donor/bromide ion donor biocide will be very good at these low ratios, it is desirable to use these biocides at Conversion Ratios of 1.0 or more, because the biocides will control the microorganisms more effectively, thereby reducing biocide usage, and because the formation of chloramines will be minimized. FIG. 1 shows at what levels the Conversion Ratio should be maintained to obtain maximum biocidal activity. However, it would not be economical, in most instances, to use products with proportions of bromide ion donor and hypochlorite donor equivalent to the desired Conversion Ratio in the recirculating water. Therefore, it is important to understand how to develop compositions and methods that allow hypochlorite donor/bromide ion donor compositions with low bromide ion donor contents to maintain the desired Conversion Ratio in the recirculating water.

#### Discovery of Bromide Ion Loss Phenomenon

During tests run on the cooling tower system described in Example 1, ACL90 PLUS (trichloroisocyanurate) was fed to the recirculating water system at a rate sufficient to maintain a free halogen concentration of 0.5 mg/L (0.5 ppm, free chlorine basis). The chlorine demand of the recirculating water system was determined to be about 282 grams of available chlorine per day. Since ACL90 PLUS, which has an available chlorine content of 90.7%, was used as the hypochlorite donor, the ACL90 PLUS requirement was 310.4 grams/day [(282÷0.907)×100%]. Sodium bromide was fed to the system at a rate of 2.6 gm NaBr/day, a rate calculated to account for blowdown loss and maintain a bromide ion concentration of 0.56 mg/L, a concentration sufficient to maintain a Conversion Ratio of one. Analyses of water samples taken from the system revealed, however, that the bromide ion was consistently as low as about 0.05 mg/L, considerably below the desired bromide ion concentration of 0.56 mg/L. Therefore, the bromide ion was lost at a rate much higher than expected.

#### Example 4

#### Demonstration of the Bromide Ion Loss Phenomenon

Tests were conducted in the following manner. The blowdown value for the recirculating water system of the cooling tower cited in Example 1 was closed to prevent the loss of water by this pathway. The recirculating water system was then dosed with enough sodium bromide to obtain a concentration of about 0.5 mg/L (0.5 ppm) of bromide ion. The free halogen was maintained at 0.5 mg/L (0.5 ppm, free chlorine basis). The water was then recirculated for about one hour to obtain a uniform concentration of bromide ion throughout the system. Water samples were then taken periodically over a 24 hour period and analyzed for bromide ion. The results of the analyses in Table 3 show that about 70% of the bromide ions were lost during this 24 hour period. Loss rates for the first few hours were actually even higher. For instance, the loss rate for the first 8.5 hours is over 6% per hour or 152% per day.

TABLE 3

Bromide Loss Data for Zero Blowdown				
Water Sample	Time (hr)	Bromide Ion Conc (ppm)	Bromide Ion Losses (%)	Lithium Conc (ppm)
1	0.0	0.50	0.0	0.42
2	8.5	0.20	54.0	0.40
3	24.0	0.13	69.0	0.41

To prove that the bromide ion losses were not due to leaks in the recirculating water system, the water was also spiked with lithium chloride at the start of this test. Lithium is not commonly found in water, can be easily analyzed for, and is not volatilized from the water system. The water samples taken for bromide analyses were also analyzed for lithium. The results shown in Table 3 demonstrate that lithium was not lost from the system during the test, thereby demonstrating that the bromide ion losses were not due to leaks, but, instead were due to other phenomena.

This example also demonstrates that the bromide ion losses can be significant in recirculating water systems, a fact not recognized by the prior art. In addition, it shows that many of the compositions described in the prior art for mixtures of hypochlorite donors and bromide ion donors actually performed as chlorine biocides instead of performing as bromine biocides like the claimed compositions. Furthermore, the results clearly indicate that without the knowledge of these losses, it would be impossible to make hypochlorite donor/bromide ion donor compositions which would perform efficiently and economically as bromine biocides.

#### Example 5

##### Compensation for Bromide Ion Loss

This example demonstrates that with knowledge of the existence of the bromide ion loss phenomena, bromide ion losses can be adequately compensated for to produce the desired results—performance of hypochlorite donor/bromide ion donor composition as bromine biocides. As shown in Example 3, prior to the discovery of the bromide ion loss phenomena, the sodium bromide was fed to the cooling water system at the rate of 2.6 grams/day, an amount only sufficient to maintain a Conversion Ratio of 0.1 (0.05 ppm divided by 0.5 ppm free chlorine), far below the ratio required to make the free halogen species perform as a bromine biocide.

The results in Examples 3 and 4 indicated that the estimated sodium bromide feed rate had to be considerably higher than the original rate (2.6 grams/day) in order to maintain a Conversion Ratio of approximately one. Tests showed that a sodium bromide feed rate of 15–17 grams/day maintained the desired bromide ion concentration. Furthermore, the biocidal system performed as bromine biocide as evidenced by the reduction in biofouling organism population from 14,000 CFU/ml for the 0.01 Conversion Ratio in Example 3 to 5000 CFU/ml.

#### Example 6

##### Determination of Appropriate Hypochlorite Donor/Bromide Ion Donor Biocide Composition by the Bromide Ion Analytical Method.

The following is an example of how this method can be applied to the determination of the appropriate hypochlorite donor compound/bromide ion donor composition for this cooling tower system.

In Example 5, the bromide ion donor (sodium bromide) requirement was determined to be 15.0–17.0 gm/day in order to maintain the bromide ion concentration at the level necessary to make the biocide perform as a bromine biocide. The hypochlorite donor/bromine ion donor composition requirement, BGC, for this particular combination was 327.4 grams/day (310.4+17.0). Therefore, the appropriate composition was 94.8% ACL90 PLUS [(310.4+327.4)×100%] and 5.2% [(17.0+327.4)×100%] sodium bromide.

If it is desired to add these two donors as a single product, the ACL90 PLUS and sodium bromide may be blended together, compacted into tablets, placed in an appropriate erosion feeder, and used to satisfy the chlorine demand and bromide ion requirements of the system. The composition would perform in the above described system as a bromine biocide. If it is desired to add the ACL90 PLUS and sodium bromide separately, the feed rates would be 310.4 and 17.0

gm/day respectively.

#### Example 7

##### Bromide Ion Loss and Composition Calculations for Cooling Towers.

An example of the procedure outlined above for calculating the total bromide ion loss and the hypochlorite donor/bromide ion donor composition required to maintain the optimum Conversion Ratio is given below. Three cooling towers, having the characteristics given in Table 4A, will be used. The three towers are various sizes and have somewhat different operating characteristics. A major difference between the three towers is the quality of the makeup water, which has a significant impact on the amount of bromide ion loss.

TABLE 4A

Characteristics of Model Cooling Towers			
Characteristic	Tower A	Tower B	Tower C
Blowdown Rate, $Q_b$ (gal/day)	1,000	2,000	12,000
Recirculation Rate, $R$ (gal/day)	200,000	600,000	$1.5 \times 10^7$
Makeup Rate, $Q_m$ (gal/day)	5,000	10,000	63,000
Desired Free Halogen Conc., FAVC (mg/L, as chlorine)	0.3	0.2	0.1
Desired Conversion Ratio, CR	1.1	0.9	1.2
Flashoff Equilibrium Coefficient, $f$	0.5	0.5	0.5
$W_L/W_G$	1.3	1.3	3.0
Tower-Top Temperature (°C.)	30	30	30
pH	8.0	8.0	8.0
Ammonia Concentration in Makeup Water (mg $NH_3$ /L)	0.0	0.1	0.1
TOC concentration in Makeup Water (mg TOC/L)	2.0	1.0	1.0
Biocide usage (grams ACL90 PLUS/day)	400	700	3,300

From the characteristics in Table 4A, the following parameters can be found for the three example towers. Sodium bromide (mol.wt.=102.90 gm/mole) is used as the bromide ion donor and ACL90 PLUS is the hypochlorite donor.

TABLE 4B

Calculated Parameters of Model Cooling Towers			
Characteristic	Tower A	Tower B	Tower C
HOBr Concentration, $C_{HOBr}$ (mg/L)	0.410	0.246	0.137
Total Br Conc, $C_{Br}$ (mg/L)	0.372	0.203	0.135
Henry's Law Constant, $H_L$	0.250	0.250	0.250
Blowdown Loss, $BrL(BD)$ , grams Br/day	1.41	1.54	6.15
HOBr Flashoff Loss, $BrL(FL)$ , grams Br/day	15.30	27.54	165.75
Bromamine Flashoff Loss, $BrL(BA)$ , grams Br/day	0.0	17.78	112.01
Organobromine Compound Formation Loss, $BrL(OBr)$ , grams Br/day	7.58	7.58	47.75
Total Bromide Ion Loss, $TBrL$ , grams Br/day	24.29	54.44	331.67
Total NaBr Needed, grams/day	31.28	70.10	427.09
% NaBr Needed in ACL90 PLUS/NaBr Composition	7.25	9.10	11.46

The above calculations show that the flashoff losses can be much larger than the blowdown loss, especially when ammonia is present. Given the values above, the appropriate composition of a trichloroisocyanuric acid/NaBr mixture is

calculated to be 7.25% NaBr for Tower A, 9.10% NaBr for Tower B and 11.46% NaBr for Tower C. If the flashoff losses and the loss due to formation of organobromine species are not accounted for, the appropriate composition would mistakenly be calculated as only 0.35% NaBr for Tower A, 0.22% NaBr for Tower B and 0.19% for Tower C.

If chlorine gas is being used as the hypochlorite donor, then the second to last line in Table 4B gives the amount of sodium bromide that must be added separately to maintain the optimum Conversion Ratio in the recirculating water.

#### Example 8

##### Determination of an Appropriate Hypochlorite Donor/Bromide Ion Donor Biocide Composition.

This example demonstrates why understanding of bromide ion loss phenomena is critical to development of commercial biocides containing both hypochlorite donors and bromide ion donors.

In this example, a cooling tower system with a recirculating water capacity of 100,000 gallons is treated with ACL90 PLUS to maintain a free available chlorine concentration of 0.5 mg/L (0.5 ppm) in the water. The daily available chlorine demand is satisfied with 11.0 pounds of ACL90 PLUS. Since the available chlorine content of ACL90 PLUS is 90.7%, 11.0 pounds of ACL90 PLUS tablets per day are equivalent to 10.0 pounds of available chlorine ( $11.0 \times 0.907 = 10.0$ ).

The ACL90 PLUS chlorine biocide can be made to perform as a bromine biocide by adding sufficient sodium bromide to the water to maintain a Conversion Ratio of at least 1.0. This requires maintenance of a bromide ion concentration in the cooling water sufficient to satisfy the stoichiometric requirements of equations (6a) and (6b). Hence, the bromide ion concentration must be 0.56 ppm ( $0.5 \text{ ppm of } \text{Cl}_2 \times M_{\text{Br}}/M_{\text{Cl}_2} = 0.5 \times 79.909/70.906 = 0.56$ ). Since the recirculating water in the example cooling tower weighs 834,000 pounds (100,000 gallons  $\times$  8.34 pounds/gallon), it must contain at least 0.47 pounds of bromide ion ( $0.56 \times 10^{-6} \times 834,000 \text{ pounds} = 0.47 \text{ pounds}$ ). This requires that the water contain a minimum of 0.605 pound of sodium bromide ( $0.47 \text{ pound} \times M_{\text{NaBr}}/M_{\text{Br}} = 0.47 \times 102.90/79.909 = 0.605$ ).

To make an ACL90 PLUS/NaBr composition perform as a bromine biocide, the composition must contain sufficient sodium bromide to build the bromide ion concentration up to and maintain it at the level required to satisfy the optimum Conversion Ratio. This can be achieved by knowing the bromide ion loss rates for the recirculating water system. If the ACL90 PLUS/NaBr product contains the exact amount of sodium bromide to compensate for the losses and maintain the Conversion Ratio at exactly one, then the sodium bromide concentration will automatically change with time until the desired concentration is reached. This occurs as follows:

When feeding a NaBr/ACL composition to a tower which initially contains no bromide ion, the bromide ion concentration will increase. The bromide ion loss rate depends on the concentration, so that the loss rate at low concentrations is very small, but slowly increases as the concentration of bromide ion increases. Thus, the initial bromide ion addition rate is larger than the bromide ion loss rate and the bromide ion concentration increases. This continues until the bromide ion loss rate matches the rate at which bromide ion is added to the system. At this point, a dynamic equilibrium condition, commonly referred to as a steady state, has been

reached. Under these conditions, the bromide ion loss rate is equal to the rate at which bromide ion is being added and no further change in the bromide ion content occurs. If the hypochlorite donor/bromide ion donor composition contained the exact amount of bromide ion to compensate for bromide ion losses at the desired steady state, that is the steady state which is eventually attained.

On the other hand, if the tower initially contains an excess of NaBr over the amount required for a Conversion Ratio of 1.0 and a NaBr/ACL mixture is used that corresponds to the desired steady state concentration, the bromide ion loss rate will be higher than the bromide addition rate. In this case, the bromide ion concentration will decrease until the loss rate and addition rate are equal and a steady state at Conversion Ratio=1.0 is reached. Again, this steady state is determined by the bromide ion addition rate, and, if the correct composition is used, the Conversion Ratio will be one at steady state.

This concept can best be visualized by considering the following information. First, in the preceding Example, 11.0 pounds of ACL90 PLUS are required to satisfy the daily chlorine demand of the cooling water. Second, 0.605 lb of sodium bromide are required to maintain the desired Conversion Ratio of 1.0. It follows that the total daily requirements for the hypochlorite donor/bromide ion donor composition, (ACL 90 PLUS/NaBr) are 11.605 pounds (11.0 + 0.605). The appropriate composition of the hypochlorite donor/bromide ion donor composition required to maintain the desired Conversion Ratio is, therefore, 94.8% ( $11.0/11.605 \times 100\% = 94.8\%$ ) ACL90 PLUS and 5.2% ( $0.605/11.605 \times 100\% = 5.2\%$ ) NaBr.

To understand how this composition can build up the bromide ion concentration to the desired level, it is necessary to consider the bromide ion addition rate and total bromide ion loss rate on an hourly basis. Again, as shown above, the total weight of bromide ion,  $W_{\text{Br}}$ , required to maintain the Conversion Ratio at 1.0 was established to be 0.47 lb at steady state. For the purpose of this Example, it is assumed that this will be the total amount of bromide ion that is lost daily. Then the total hourly bromide ion loss rate (all pathways),  $\text{HTBrL}$ , is simply  $W_{\text{Br}}$  divided by 24 hours. This corresponds to a rate of 0.01958 lb/hr ( $0.47 \text{ lb} \div 24 \text{ hr} = 0.01958$ ). With respect to  $W_{\text{Br}}$ , the percent total hourly bromide ion loss rate,  $\text{PHTBrL}$ , is, as determined by equation (25), 4.2% ( $0.01958/0.47 \times 100\% = 4.2\%$ ).

$$\text{PHTBrL} = \frac{\text{HTBrL}}{W_{\text{Br}}} \times 100\% \quad (25)$$

This percent total hourly loss rate corresponds to a percent total daily loss rate of 100%. It is important to remember that it is entirely possible for percent total daily loss rate to be greater than 100%.

With regards to the bromide ion addition rate, it was established previously that 0.605 lb of sodium bromide are required to satisfy the Conversion Ratio conditions specified. The hourly sodium bromide addition rate is thus 0.02521 lb/hr ( $0.605 \text{ lb} \div 24 \text{ hr}$ ). In terms of bromide ion, the total hourly addition rate is 0.01958 lb/hr ( $0.02521 \text{ lb NaBr/hr} \times M_{\text{Br}}/M_{\text{NaBr}} = 0.02521 \times 80/103 = 0.01958$ ).

It follows that at the end of the first hour of use of the ACL90 PLUS/NaBr composition the bromide ion content of the water will be 0.01958 pounds minus the amount of bromide ion losses. Since the total hourly loss rate is 4.2%/hr, the amount of bromide ion lost in the first hour is only 0.00082 lb ( $0.042 \times 0.01958$ ). The bromide ion content

at the end of the first hour is thus 0.01876 lb (0.01958-0.00082). At the end of the second hour, another 0.01958 lb of bromide will have been added bringing the gross amount to 0.03834 (0.01876+0.01958) lb. However, the bromide ion loss is slightly higher and amounts to approximately 0.00161 lb (0.03834×0.0420). The net amount of bromide ion remaining has now increased to 0.03673 lb (0.03834-0.00161). Thus, with each successive addition of sodium bromide, the bromide ion concentration will continue to increase, but at the same time, the bromide ion loss rate will increase. Eventually, the loss rate will catch up with the addition rate and the two rates will be essentially equivalent thereafter. At this point, steady state conditions have been attained and subsequent ACL90 PLUS/NaBr additions merely maintain the Conversion Ratio at the desired level, in this case, 1.0.

A further refinement of these calculations is to determine the hourly bromide ion losses by the various pathways, since blowdown losses apply to all bromine species but losses by flashoff of hypobromous acid and bromamines and the formation of organobromine compounds apply only to the hypobromite species. This is achieved with equations (26) and (27). The percent hourly bromide ion loss rate by blowdown, PHBrL(BD), is calculated by equation (26).

$$PHBrL(BD) = \frac{BrL(BD)}{C_{Br} \times V_w} \times \frac{1000}{24} \times 100\% \quad (26)$$

where:

PHBrL(BD)=the percent of bromide ion lost by blowdown, %/hr

BrL(BD)=as defined in equation (9)

$C_{Br}$ =as defined in step (3) of "calculation of losses method"

$V_w$ =volume of recirculating water, L

1000=conversion factor, grams to milligrams

24=conversion factor, days to hours

The percent hourly loss of bromide ion by the other pathways (flashoff of hypobromous acid and bromamines and formation of organobromine compounds) is specifically proportional to the amount of hypobromite species in the recirculating water. The percent hourly loss of hypobromite species by these pathways, PHOBrL, is calculated with equation (27).

$$PHOBrL = \frac{[TSrL - BrL(BD)]}{C_{HOBr} \times V_w} \times \frac{M_{HOBr}}{M_{Br}} \times \frac{1000}{24} \times 100\% \quad (27)$$

where:

PHOBrL=percent of hypobromite species lost by pathways other than blowdown, %/hr

TSrL=as defined in equation (23)

BrL(BD)=as defined in equation (9)

$C_{HOBr}$ =as defined in step (2) of "calculation of losses method"

$V_w$ =volume of recirculating water, L

$M_{HOBr}$ =mole weight of hypobromous acid, gm

$M_{Br}$ =mole weight of bromide ion, gm

1000=conversion factor, grams to milligrams

24=conversion factor, days to hours

PHOBrL is essentially the weight of hypobromite species lost per hour divided by the weight of hypobromite species contained in the recirculating water. With equation (25), the

percent total hourly bromide ion loss rate, PHTBrL, was calculated to be 4.2%/hr. These refinements account for what fraction of bromide ion losses are due to blowdown and the other pathways. To illustrate the refinements of the calculations, the losses due to blowdown, PHBrL(BD), and the losses by other pathways, PHOBrL, are taken to be 0.83%/hr and 3.33%/hr, respectively, for FIGS. 2-5.

These calculations can be used to illustrate the interrelationship between the concentration of the bromide ion in the recirculating water and the composition of the hypochlorite donor/bromide ion donor compositions. They were utilized to generate the graphs shown in FIGS. 2-5 which illustrate the effect of the biocide composition on the buildup of bromide ion with time and the ability of the composition to attain the optimum Conversion Ratio at steady state conditions. Since these calculations simulate the dynamics of the bromide ion content of water recirculation systems, they can be used to determine the composition required to produce the desired Conversion Ratio once the PHBrL(BD) and PHOBrL have been determined. FIG. 6 illustrates the effect of bromide ion loss rate on the composition required for the preferred range of Conversion Ratios. Therefore, it illustrates, in conjunction with the following examples, how the various compositions are able to perform as bromine biocides.

#### Example 9

##### Buildup of Bromide Ion to Steady State Concentration with a 2% NaBr/98% ACL90 PLUS Composition.

The cooling tower in Example 8 is initially treated with 11.0 pounds of ACL90 PLUS per day to maintain a free chlorine concentration of 0.5 mg/L, thus the tower initially contains no bromine containing species. The biocide is then switched to a composition of 2% NaBr and 98% ACL90 PLUS. FIG. 2 presents the calculated bromide ion content in terms of sodium bromide of the tower versus the time elapsed since starting the NaBr/ACL90 PLUS composition, given that PHOBrL=3.33%/hour (80%/day) and that PHBrL(BD)=0.83%/hour (20%/day). It shows how the total amount of bromine containing species (given as pounds of NaBr) contained in the recirculating water system builds up with time during the initial few days of use of the 2.0% NaBr/98% ACL90 PLUS composition until a steady state concentration is reached after about three days. At steady state, the tower in FIG. 2 contains about 0.2 pounds of NaBr, which is considerably below the 0.605 pounds of NaBr required for a Conversion Ratio of 1.0, as shown by the line labeled "CR=1.0". In this case, the free halogen is a mixture of hypochlorite species and hypobromite species and the killing efficiency is less than ideal.

#### Example 10

##### Buildup of Bromide Ion to Steady State Concentration with a 9% NaBr/91% ACL90 PLUS composition.

FIG. 3 shows the case where a NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition with a much higher percentage of NaBr (9.0%) is fed into the tower described in Example 8. As in Example 9, the bromide ion content of the tower builds up smoothly until a steady state is reached. In this case, however, steady state is reached in about 20 days. The steady state NaBr content is 3.0 pounds and the steady state Conversion Ratio is 5.0. In this case, all of the free

halogen is present as hypobromite species and the killing efficiency is very high, but a considerable excess of bromide ion is present which is wasted.

#### Example 11

##### Buildup of Bromide Ion to Steady State Concentration with the Optimum 5.2% NaBr/94.8% ACL90 PLUS Composition.

FIG. 4 shows the ideal case for the tower described in Example 8, where PHBrL(BD) is 0.83%/hour (20%/day) and PHOBrL is 3.33%/hour (80%/day). A Conversion Ratio of 1.0 is achieved after about three days and then maintained at steady state conditions by feeding a composition of 5.2% NaBr/94.8% trichloroisocyanuric acid. This composition therefore performs as a bromine biocide in this tower with very little excess bromide ion being required.

#### Example 12

##### Buildup of Bromide Ion to Steady State Concentration with BCDMH

FIG. 5 shows the case for BCDMH, which has a bromide and available halogen content equivalent to about 40% NaBr/60% trichloroisocyanuric acid, in the tower of Example 8. The steady state Conversion Ratio (for PHOBrL=3.33%/hour and PHBrL(BD)=0.83%/hour) which is attained after about 20 days is 56.7. This is a tremendous waste of bromide ion, since 56.7 times as much bromide is used as is necessary to maintain the maximum killing efficiency. This high Conversion Ratio for BCDMH is confirmed by the data in Example 1, Table 1, where a Conversion Ratio of 41.1 was determined experimentally for BCDMH in a tower with somewhat different characteristics. The waste of bromide is even greater for cases where PHOBrL and PHBrL(BD) are lower than used in this example.

#### Example 13

##### Hypochlorite Donor/Bromide Ion Donor Compositions Required For Specific Steady State Conversion Ratios

The relationship between the sum of PHBrL(BD) and PHOBrL and the required composition of a NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition is summarized in FIG. 6. The line labeled 'CR=1.0' gives the relationship between PHBrL(BD)+PHOBrL and the weight % NaBr required in the composition to produce a Conversion Ratio of 1.0. For instance, for a tower with a bromide ion loss rate of 3.3%/hour the NaBr/trichloroisocyanuric acid composition should be 4.8% NaBr. The lines marked 'CR=4.0' and 'CR=0.5' give the relationship for the extremes of the most preferred Conversion Ratio. The dashed arrow at 4% NaBr shows that a composition of 4% NaBr/96% trichloroisocyanuric acid can maintain the Conversion Ratio in the most preferred range of 0.5 to 4.0 for towers for PHBrL(BD)+PHOBrL=0.75%/hour to well over 5%/hour. This range covers virtually all common cooling tower systems. In contrast, a composition with only 2% NaBr/98% trichloroisocyanuric acid will maintain the Conversion Ratio in the most preferred range only for PHBrL(BD)+PHOBrL between 0.38 and 2.5%/hour. Many common cooling towers have larger bromide ion loss rates than this, as was shown in Examples 3 and 4.

This example shows the importance of understanding the relationship between the total bromide ion loss rate and the sodium bromide content of ACL90 PLUS/NaBr compositions and the capabilities of these compositions to attain and maintain the desired Conversion Ratios, especially those that enable these compositions to perform as bromine biocides. These same relationships also exist for other hypochlorite donor/bromide ion donor compositions and/or combinations. These relationships can be established with the methods described herein.

For cooling tower operations subject to EPA discharge limits of 0.2 ppm (available chlorine basis), it is preferred to maintain the Conversion Ratio at or above one, since hypobromite species dissipate faster than hypochlorite species.

For use in air washers, it is preferred that the Conversion Ratio be maintained at or above a value of one since it is important to eliminate all chlorine or chloramine odors from the air passed through the air washer. Odor is more important in air washers than in cooling towers since the washed air is used inside buildings, factories, and the like. Thus, somewhat higher percentages of NaBr are required for compositions of this invention used in cooling tower operations subject to EPA limits and in air washers. For instance, FIG. 6 shows that a 4% NaBr/96% trichloroisocyanuric acid composition will maintain the Conversion Ratio in the preferred range of 1.0 to 4.0 for PHBrL(BD)+PHOBrL=0.75% to 2.75%/hour. If the loss rate is higher, a composition with a higher NaBr percentage would be necessary.

#### Example 14

##### Demonstration of Bromide Ion Loss From Spas

This example demonstrates the magnitude of bromide ion loss that can occur in a commercial spa. A spa with a capacity of 1000 gallons of water was chlorinated continuously with ACL90 PLUS (trichloroisocyanuric acid) around the clock to maintain a free chlorine concentration of 2 ppm. The spa water was maintained at a temperature of 40° C. The water was aerated only during the day, the high bather load period, for about 12 hours. Sufficient sodium bromide was added to the spa water to obtain a bromide ion concentration of 3 ppm. This is the amount required to attain a Conversion Ratio of 1.33 versus the optimum of 1.0 and to make the chemicals perform as a bromine sanitizer. Water samples were taken about every four hours for several days. The analyses showed that the bromide ion concentration decreased steadily from 3 to 1 ppm over a period of 6 days. The chlorine demand was about 10 ppm per day (available chlorine basis). During this period, the odor of the air above the spa changed gradually from that of bromamines to chloramines. These results demonstrated that bromide ion was lost from the water and that the hypohalite species were a mixture of hypochlorite and hypobromite species. As a consequence, the biocide performed more like a chlorine sanitizer than a bromine sanitizer.

#### Example 15

##### Control of Optimum Conversion Ratio in Spas with ACL90 PLUS/NaBr Compositions

This example further demonstrates how knowledge of the bromide ion loss can be applied to the development of the appropriate sanitizer compositions. The results in Example 14 show that the bromide ion loss rate was about 0.33 ppm/day. This means that at least 2.5 grams must be added daily to maintain the desired concentration. The chlorine

demand during this period was about 10 ppm/day, which corresponds to a ACL90 PLUS consumption rate of 41.3 grams/day. These results indicate that to satisfy the chlorine demand and bromide ion loss requirements with a product made of the two materials, the product must contain ACL90 PLUS and sodium bromide in the weight proportions of 41.3 to 2.5. Thus, the tablet for this application must contain at least 94.3 wt % ACL90 PLUS and 5.7 wt % sodium bromide.

To demonstrate the utility of this concept, an ACL90 PLUS/sodium bromide mixture with 6% NaBr was compacted into one-inch tablets weighing 15 grams each. The tablets were placed in a standard erosion feeder where the water flow was adjusted to maintain the desired free halogen concentration of 2 ppm (available chlorine basis). Water samples were then taken periodically for six days. The bromide analyses showed that the bromide ion concentration built up steadily to the desired concentration and remained constant for the remainder of the test, thereby insuring that this product was performing as a bromine sanitizer.

#### Bromine Volatilization Suppressant

It has also been discovered that, in addition to simply adding enough bromide ion donor to compensate for all bromide ion losses, it is possible to approach the problem in a second way, that is, by reducing or suppressing the amount of volatilization of HOBr and bromamines. This can be accomplished by addition of a hypobromous acid volatilization suppressant compound. The volatilization suppressant must bind free bromine species (HOBr) strongly enough to reduce the concentrations of hypobromous acid and bromamine significantly, but not so strongly that the disinfecting properties of the bromine-based biocide will be reduced. In addition, the volatilization suppressant must be chemically compatible with the hypochlorite donor compounds in the single product compositions to be fed to the tower.

Cyanuric acid has been used in swimming pools to reduce the decomposition of hypochlorous acid by the UV rays of sunlight and in cooling towers to reduce the loss of free chlorine. However, cyanuric acid will not suppress the loss of free bromine by volatilization and degradation in sunlight because cyanuric acid does not bind free bromine as strongly as it does free chlorine.

It has been found that hydantoin derivatives (such as DMH); sulfonamide derivatives; sulfamic acid derivatives; glycoluril derivatives; oxazolidinone derivatives; imidazolidinone derivatives; and succinimide derivatives are capable of acting as volatilization suppressants for free bromine. However, it was discovered that when hydantoin derivatives are used, the concentration of the volatilization suppressant relative to the concentration of the free bromine must be controlled in order to avoid significant reduction in the biocidal activity of the biocides of the present invention.

DMH can be used to reduce bromide ion losses by reducing volatilization loss by as much as 85% before it begins to have a deleterious effect on the disinfection properties of the bromine-based biocide according to the present invention. However, DMH concentrations more than ten times the hypobromous acid concentration (expressed in terms of free available chlorine) can significantly decrease the biocidal effectiveness of the hypobromous acid. For example, if the free halogen level in the recirculating water is controlled at 0.5 mg/L (free available chlorine basis), DMH concentrations greater than 5.0 mg/L must be avoided.

DMH concentrations of over 50 mg/L can easily be reached if BCDMH is used as the biocide. Because of the potential for reducing the effectiveness of bromine-based biocides, the concentration of DMH or other stabilizer compounds should be maintained at an appropriately low level, preferably less than 10 ppm in the case of DMH.

#### Example 16

##### Demonstration of the Effect of Dimethylhydantoin on Bromide Ion Losses

This example demonstrates how bromide ion losses can be significantly reduced with bromine volatilization suppressants.

In this particular experiment, the cooling water of Example 4 was dosed with enough sodium bromide to obtain a Conversion Ratio of about one. DMH was then added to the water in an amount sufficient to attain a concentration of 20 ppm. Again, lithium chloride was used as a tracer. The water was recirculated for about one hour to obtain a uniform distribution of chemicals. Water samples were then taken periodically for the next 24 hours and analyzed for bromide, lithium and DMH. The results are tabulated in Table 5.

TABLE 5

Effect of DMH on Bromide Ion Losses					
Water Sample	Time Hr.	Bromide Ion Concentration ppm	DMH Concentration ppm	Lithium Concentration ppm	Bromide Ion Losses (%)
1	1	0.5	21	0.45	0
2	2	0.5	20	0.44	0
3	3	0.5	19	0.42	0
4	4	0.48	20	0.42	4
5	8	0.46	20	0.42	8
6	16	0.42	19	0.41	18
7	24	0.38	18	0.42	24

These data demonstrate that bromide ion losses were reduced dramatically with the addition of DMH, thus establishing another way to compensate for bromide ion losses via the volatilization pathway.

#### Example 17

##### Effect of DMH on Henry's Law Constants for Hypobromous Acid

The previous example demonstrated that DMH could be used to obtain significant reductions in bromide ion losses from cooling water systems containing the hypochlorite donor/bromide ion donor compositions described in this invention. This example shows the effect of the DMH concentration on the tendency of the bromide ion to be lost from cooling waters by volatilization. Just as important, it provides data critical to controlling the DMH concentration so that the excellent biocidal properties of these bromine biocide compositions are not compromised by high DMH residuals.

The effect of DMH concentration was demonstrated by determining the Henry's Law constants for a series of solutions in which the available halogen, bromide, pH and temperature were held constant but the DMH concentration was varied.

The results of these experiments are tabulated in Table 6 and shown graphically in FIG. 7.

TABLE 6

Effect of DMH on Henry's Law Constants For Solutions Containing Hypohalite Species and Bromide Ion Experimental Conditions	
pH = 8.5	
Temperature = 22.5° C.	
Free halogen (as Cl <sub>2</sub> ) = 2 mg/L	
Bromide ion = 2.25 mg/L	
DMH/Free Bromine Mole Ratio	Henry's Law Constant H <sub>k</sub>
0.0	0.220
2.0	0.037
5.0	0.028
10.0	0.024
30.0	0.019

Depicting these results graphically, FIG. 7 shows that the Henry's Law constant decreased significantly as the DMH/free bromine mole ratio increased from 0 to 10, but decreased very little above 10. These results indicate that there is no need to use DMH/free bromine ratios of greater than 10. More importantly, killing efficiency data show that the biocidal properties begin to decrease significantly above this ratio.

The foregoing description has been directed to particular embodiments of the invention for the purposes of illustration and explanation. It will be apparent, however, to those skilled in this art that many modifications and changes in the compositions and methods set forth will be possible without departing from the scope and spirit of the invention. It is intended that the following claims be interpreted to embrace all such modifications and changes.

What is claimed is:

1. A solid biocidal composition for use in recirculating water systems comprising a hypochlorite donor, a bromide ion donor, and a bromine volatilization suppressant

wherein the composition contains a biocidally effective amount of the bromide ion donor to make the composition perform as a bromine biocide in said recirculating water system and to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of at least about 0.2 to about 20; and

wherein the hypochlorite donor is sodium dichloro-s-triazinetrioxide; the bromide ion donor is sodium bromide, and the bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin; unsubstituted, halogenated or alkylated sulfonamide; unsubstituted, halogenated or alkylated sulfamic acid; unsubstituted, halogenated or alkylated glycoluril; unsubstituted, halogenated or alkylated succinimide; unsubstituted, halogenated or alkylated oxazolidinone; or unsubstituted, halogenated or alkylated imidazolidinone.

2. The biocidal composition according to claim 1 wherein said bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin or unsubstituted, halogenated or alkylated glycoluril.

3. The biocidal composition according to claim 2 wherein said bromine volatilization suppressant is a halogenated dimethylhydantoin or a halogenated glycoluril.

4. The biocidal composition according to claim 3 wherein said bromine volatilization suppressant is a chlorinated or brominated dimethylhydantoin.

5. The biocidal composition according to claim 3 wherein said bromine volatilization suppressant is a chlorinated or brominated glycoluril.

5 6. The biocidal composition according to claims 2, 3, 4 or 5 comprising

from about 85 parts by weight to about 98 parts by weight hypochlorite donor;

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

10 from about 1 part by weight to about 10 parts by weight bromine volatilization suppressant.

7. The biocidal composition according to claims 1 or 2 wherein said composition is in the form of a granular mixture.

8. A method of controlling biofouling and microorganism population levels in a recirculating water system comprising (a) determining the rate of loss of bromide ion from the system due to blow-down, volatilization and formation of stable organobromine compounds; and (b) adding, in a biocidally effective amount to provide prolonged and controlled release of hypobromous acid and to maintain the mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water in the range of at least about 0.2 to about 20, a solid biocidal composition comprising a hypochlorite donor, a bromide ion donor in amounts sufficient to make said composition perform as a bromine biocide in said recirculating water system, and a bromine volatilization suppressant

(i) wherein said hypochlorite donor is sodium dichloro-s-triazinetrioxide;

(ii) wherein said bromide ion donor is sodium bromide; and

(iii) wherein said bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin; unsubstituted, halogenated or alkylated sulfonamide; unsubstituted, halogenated or alkylated sulfamic acid; unsubstituted, halogenated or alkylated glycoluril; unsubstituted, halogenated or alkylated succinimide unsubstituted, halogenated or alkylated oxazolidinone; or unsubstituted, halogenated or alkylated imidazolidinone.

9. The method according to claim 8, wherein the bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin or unsubstituted, halogenated or alkylated glycoluril.

10. The method according to claim 9, wherein the bromine volatilization suppressant is a halogenated dimethylhydantoin or a halogenated glycoluril.

11. The method according to claim 10, wherein the bromine volatilization suppressant is a chlorinated or brominated dimethylhydantoin.

12. The method according to claim 10, wherein the bromine volatilization suppressant is a chlorinated or brominated glycoluril.

13. The method according to claims 9, 10, 11 or 12 wherein said biocidal composition comprises:

from about 85 parts by weight to about 98 parts by weight hypochlorite donor;

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

from about 1 part by weight to about 10 parts by weight bromine volatilization suppressant.

14. The method according to claims 8 or 9, wherein said composition is in the form of a granular mixture.



15. A solid biocidal composition for controlling biofouling and microorganism population levels in recirculating water systems that provides hypobromous acid when immersed in water, comprising a hypochlorite donor, a bromide ion donor in amounts sufficient to make said composition perform as a bromine biocide in said recirculating water system, and a bromine volatilization suppressant:

- (i) wherein said hypochlorite donor is sodium dichloro-s-triazinetriene;
- (ii) wherein said bromide ion donor is sodium bromide; and
- (iii) wherein said bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin; unsubstituted, halogenated or alkylated sulfonamide; unsubstituted, halogenated or alkylated sulfamic acid; unsubstituted, halogenated or alkylated glycoluril; unsubstituted, halogenated or alkylated succinimide; unsubstituted, halogenated or alkylated oxazolidinone; or unsubstituted, halogenated or alkylated imidazolidinone.

16. The biocidal composition according to claim 15 wherein said bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin or unsubstituted, halogenated or alkylated glycoluril.

17. The biocidal composition according to claim 16 wherein said bromine volatilization suppressant is a halogenated dimethylhydantoin or a halogenated glycoluril.

18. The biocidal composition according to claim 17 wherein said bromine volatilization suppressant is a chlorinated or brominated dimethylhydantoin.

19. The biocidal composition according to claim 17 wherein said bromine volatilization suppressant is a chlorinated or brominated glycoluril.

20. The biocidal composition according to claims 15, 16, 17, 18 or 19 comprising

from about 85 parts by weight to about 98 parts by weight hypochlorite donor;

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

from about 1 part by weight to about 10 parts by weight bromine volatilization suppressant.

21. The biocidal composition according to claims 15 or 16 wherein said composition is in the form of a granular mixture.

22. A method of providing biocidal control in a recirculating water system comprising adding to the recirculating water system a hypochlorite donor, a bromide ion donor and a bromine volatilization suppressant,

- (i) wherein said hypochlorite donor is sodium dichloro-s-triazinetriene;
- (ii) wherein said bromide ion donor is sodium bromide; and
- (iii) wherein said bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin; unsubstituted, halogenated or alkylated sulfonamide; unsubstituted, halogenated or alkylated sulfamic acid; unsubstituted, halogenated or alkylated glycoluril; unsubstituted, halogenated or alkylated succinimide; unsubstituted, halogenated or alkylated oxazolidinone; or unsubstituted, halogenated or alkylated imidazolidinone.

23. The method according to claim 22, wherein the bromine volatilization suppressant is selected from the group consisting of unsubstituted, halogenated or alkylated hydantoin or unsubstituted, halogenated or alkylated glycoluril.

24. The method according to claim 23 wherein said bromine volatilization suppressant is a halogenated dimethylhydantoin or a halogenated glycoluril.

25. The method according to claim 24 wherein said bromine volatilization suppressant is a chlorinated or brominated dimethylhydantoin.

26. The method according to claim 24 wherein said bromine volatilization suppressant is a chlorinated or brominated glycoluril.

27. The method according to claim 22, 23, 24, 25 or 26 comprising

from about 85 parts by weight to about 98 parts by weight hypochlorite donor;

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

from about 1 part by weight to about 10 parts by weight bromine volatilization suppressant.

28. The method according to claim 22 or 23 wherein said hypochlorite donor, bromide ion donor and bromine volatilization suppressant are added in the form of a granular mixture.

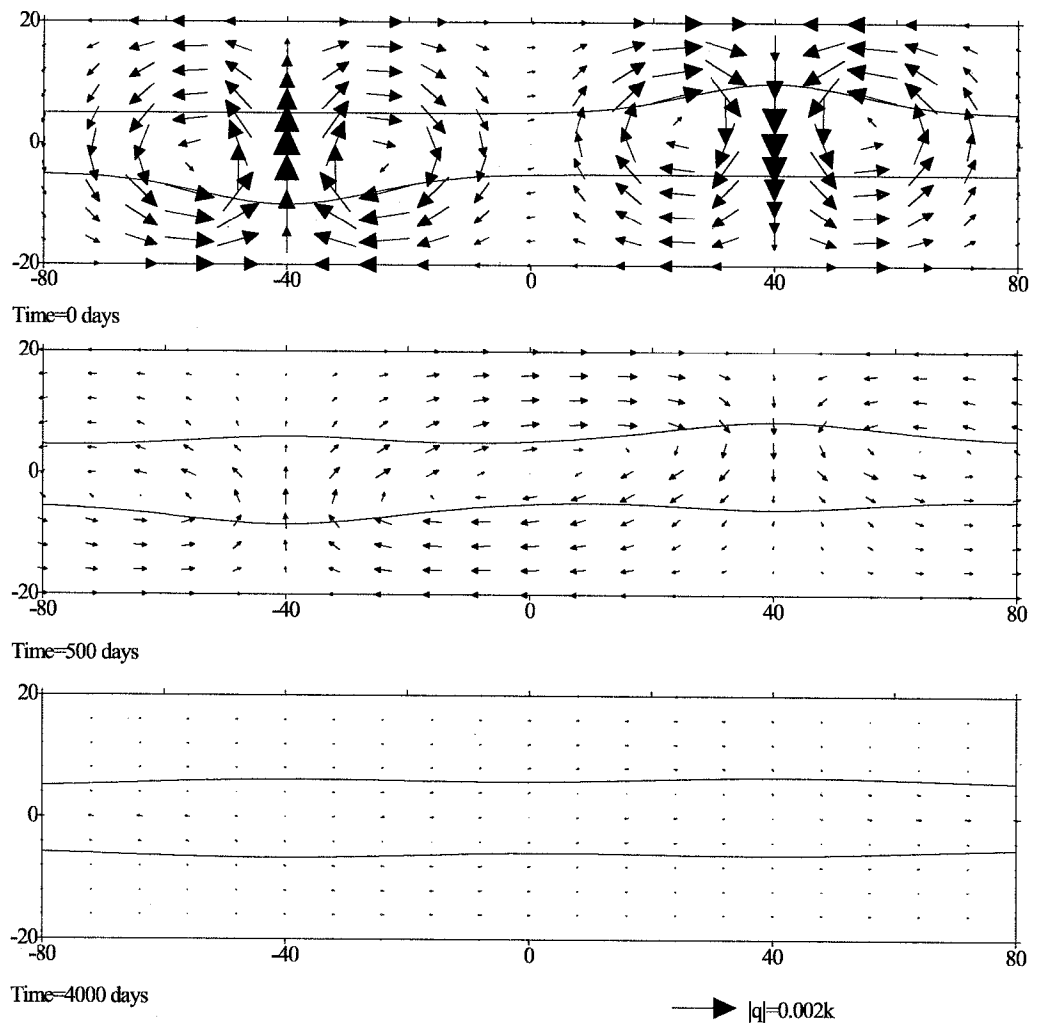
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# APPENDIX

## C



# Analytic Element Modeling of Coastal Aquifers



# Introduction

## Motivation

Salt water intrusion is a potential threat to drinking water supplies in the coastal areas of the USA. Cities along the coast are increasing their pumping of groundwater to support a rising population. The increased pumping may result in an increase of chlorides in the well water due to the upconing of brackish groundwater. Even a small concentration of chlorides will give the water a salty taste; water tastes salty to most people if the concentration of chlorides is 0.25 g/l or greater. Sea water, on the other hand, contains about 18 grams of chlorides per liter. The maximum guideline concentration set by the World Health Organization is 0.25 grams of chlorides per liter. The potential upconing of brackish groundwater may be studied by the simulation of groundwater flow with a numerical model.

Groundwater flow in coastal aquifers is affected by the difference in density between fresh and salt water. The fresh water is separated from the salt water through a brackish transition zone, in which the salinity (and thus the density) of the water varies from that of salt water to that of fresh water. If the transition zone is relatively thin, the transition from fresh to salt water may be modeled as an abrupt one: the fresh water is separated from the salt water by an interface. If this is not the case, the effect of the variation in density on the flow in the transition zone must be taken into account. The modeling of the flow generated by variations in density, the variable density flow, is the subject of this report. Specifically, it is investigated whether groundwater flow in coastal aquifers can be modeled under the Dupuit approximation in combination with analytic elements.

## Background

Numerous numerical models are available to simulate variable density flow for both two-dimensional flow in the vertical plane and three-dimensional flow. The flow field may be modeled with the finite-element method or the finite-difference method while the solute transport equation may also be solved by the random walk method or the method of characteristics. Two-dimensional models include SUTRA (Voss, 1984), and MOCENSE (Sanford and Konikow, 1985), the variable density version of MOC (Konikow and Bredehoeft, 1978). Three-dimensional models include HST3D (Kipp, 1986) and SWICHA (Lester, 1991). Maas and Emke (1988) developed a procedure to simulate variable density flow with numerical models for single

# APPENDIX D

Current Technology of  
**Chlorine Analysis**  
for Water and Wastewater

Technical Information Series — Booklet No.17  
By **Danial L. Harp**

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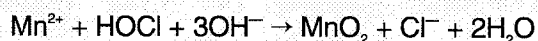
# Current Technology of Chlorine Analysis for Water and Wastewater

Table of Contents	Page
1. Overview of Chlorine Chemistry in Water Treatment .....	1
2. Analytical Methods for Chlorine and Chloramines .....	2
a. DPD Colorimetric Method .....	2
b. DPD Titration Method .....	5
c. Iodometric Titration Method.....	6
d. Amperometric Titration Methods .....	6
e. Other Analytical Methods: .....	8
Orthotolidine.....	8
Syringaldazine (FACTS) .....	9
Electrode .....	9
3. Method Interferences and Sources of Errors .....	11
a. Sampling Considerations .....	11
b. Interferences Common to All Chlorine Methods .....	11
Other Disinfectants.....	11
Manganese Compounds.....	12
Organic Chloramines .....	12
Bromides in Chlorinated Waters .....	12
c. Errors Common to Total Chlorine Determinations .....	12
d. Interferences in the DPD Methods.....	13
Calibration Non-Linearity .....	13
Precautions in Using Permanganate as an Equivalent Standard .....	13
Monochloramine Interference in the Free Chlorine Test .....	15
Stability of the Colored Reaction Product .....	16
Compensation for Sample Color and Turbidity .....	16
e. Interferences in the Amperometric Titration Methods .....	17
Deposition on Electrode Surfaces .....	17
Manganese Interference.....	17
Nitrite Interference .....	17
Choice of Reductant.....	19
Effect of Iodine Demand on End Point Determinations .....	19
Order of Reagent Addition.....	20
4. Method Comparisons and Performance Evaluations .....	21
a. Field Kit or Laboratory Comparisons .....	21
b. Performance Evaluations of Residual Chlorine Process Analyzers .....	23
5. Selection of the Appropriate Testing System .....	24
a. Field Testing .....	24
b. Laboratory Testing .....	25
c. On-line Automated Testing .....	26
6. Conclusions .....	27
References .....	29
Acknowledgements .....	30

analyte, due to the extra time involved or changes of reaction conditions for the test.

#### **Manganese Compounds**

Manganese can exist in oxidation states of +2 through +7. The higher oxidation states, typically +3 to +7, will interfere with all the common chlorine methods. Free chlorine reacts to oxidize soluble manganese compounds. For example:



Apparently, chloramines will not oxidize manganous compounds. Oxidized manganese will react directly with the DPD indicator. It is claimed that Mn (+4) does not interfere in the FACTS method at a 1.0 mg/L level (*Ref. 3.2*). At 2.6 mg/L Mn (+4), interference is noted after five minutes with the FACTS test. Oxidized manganese (+4 to +7) also will interfere in the amperometric titration for free chlorine.

Iodide can be oxidized by Mn (+4 to +7) to  $\text{I}_2$ , which will interfere in both the colorimetric and titrimetric methods for total chlorine. The interference of oxidized manganese in back-titration methods appears to be a function of iodide concentration and the test pH (*Ref. 3.3*).

The customary procedure to compensate for manganese interference in the DPD methods is to first dechlorinate the sample with sodium arsenite, which does not affect the manganese, and then proceed with the test. The result obtained with the dechlorinated sample is subtracted from the normal test result to obtain the correct chlorine concentration. Unfortunately, alternative reducing agents, such as PAO, thiosulfate, or ferrous salt, cannot be used because they also will reduce Mn (+7).

#### **Organic Chloramines**

There is considerable debate over the interference of organic chloramine compounds with the cited free chlorine tests. Organic nitrogen compounds can combine with chlorine analogous to the reaction with ammonia:



where R = the organic moiety

Typical organic nitrogen compounds would include common amino acids and heterocyclic bases. Free chlorine reacts quickly with these types of compounds to form non-germicidal organic chloramines.

Published studies (*Refs. 3.4, 3.5*) have concluded that certain organic chloramines, especially N-chlorinated

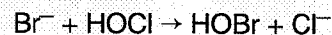
amino acids and N-chlorinated heterocyclic compounds, will interfere with all the common analytical methods for free chlorine. However, chlorinated amino acids do not appear to interfere in the free chlorine DPD and FACTS methods.

White (*Ref. 3.6*) has contested the validity of organic chloramine interference in the amperometric titration method. Based on his observations and surveys of wastewater disinfection systems, he contends that organic chloramines will be detected only as the dichloramine fraction when titrated in a forward amperometric titration.

At this time, the interference of organic chloramines in the free chlorine tests must be considered conditional, pending additional research.

#### **Bromide in Chlorinated Waters**

Sea water and estuary water may contain natural levels of bromide ions up to 65 mg/L. The addition of chlorine to waters containing bromide will produce hypobromous acid and hypobromite ion:



This reaction is irreversible and the product will interfere with all common analytical procedures for free chlorine.

If ammonia is present in the sample, HOBr will react with ammonia forming bromamines. Bromamines will react with iodide reagent analogously to the chloramine reaction, indicating a positive interference in the total chlorine test.

It should be noted that bromide, when present in a chlorinated sample, forms a disinfectant (hypobromite and/or bromoamines) and, technically, the analytical results would indicate the total oxidizing capacity of the sample.

#### **3c. Errors Common to Total Chlorine Determinations**

All of the common total chlorine methods are based on the oxidation of iodide to triiodide ion. There are several potential sources of errors related to the iodide/triiodide reaction. They include:

- air oxidation of the iodide reagent
- volatilization of produced iodine
- iodine or iodate contamination in the iodide reagent
- consumption of triiodide by sample components.



# APPENDIX

## E



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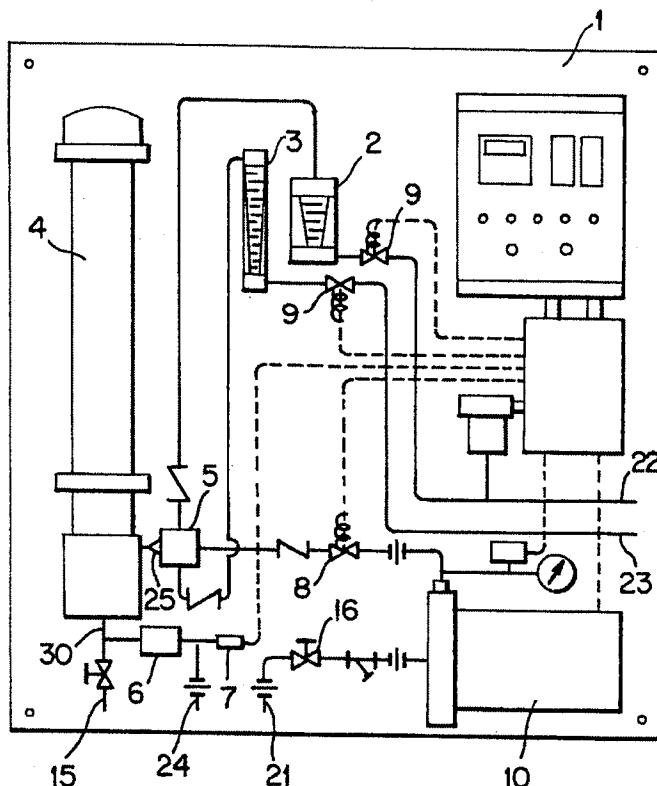
**United States Patent** [19]**Kelley**[11] **Patent Number:** **5,516,501**[45] **Date of Patent:** **May 14, 1996**[54] **PROCESS FOR THE PREPARATION OF  
AQUEOUS SOLUTIONS OF BROMINE  
BASED DISINFECTANTS**[75] **Inventor:** **Joseph M. Kelley, Westfield, N.J.**[73] **Assignee:** **International Dioxide, Clark, N.J.**[21] **Appl. No.:** **411,410**[22] **Filed:** **Mar. 28, 1995****Related U.S. Application Data**[63] Continuation of Ser. No. 76,278, Jun. 11, 1993, abandoned,  
which is a continuation of Ser. No. 878,773, May 5, 1992,  
abandoned.[51] **Int. Cl.<sup>6</sup>** ..... **C01B 11/20**[52] **U.S. Cl.** ..... **423/473; 210/754**[58] **Field of Search** ..... **423/473; 210/754,  
210/756, 764**[56] **References Cited****U.S. PATENT DOCUMENTS**

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3rd ed. 1976, pp. 244-251.Perry et al, "Chemical Engineers' Handbook", Fifth ed. TP  
155 p. 4 1973.**Primary Examiner**—Gary P. Straub**Assistant Examiner**—N. M. Nguyen**Attorney, Agent, or Firm**—Rogers & Wells[57] **ABSTRACT**

Processes for preparing a relatively concentrated aqueous solution of about 700–3000 ppm hypobromous acid are provided. Hypochlorous acid solutions are prepared by either reacting chlorine gas with water or sodium hypochlorite with an acid. The resulting hypochlorous acid is then reacted with an alkali metal or alkaline earth bromide in order to form the hypobromous acid. Critical parameters are pH, Br/Cl mole ratio, and chlorine concentration. Under optimum conditions, substantially 100% conversion of bromide to hypobromous acid can be attained.

**19 Claims, 4 Drawing Sheets**

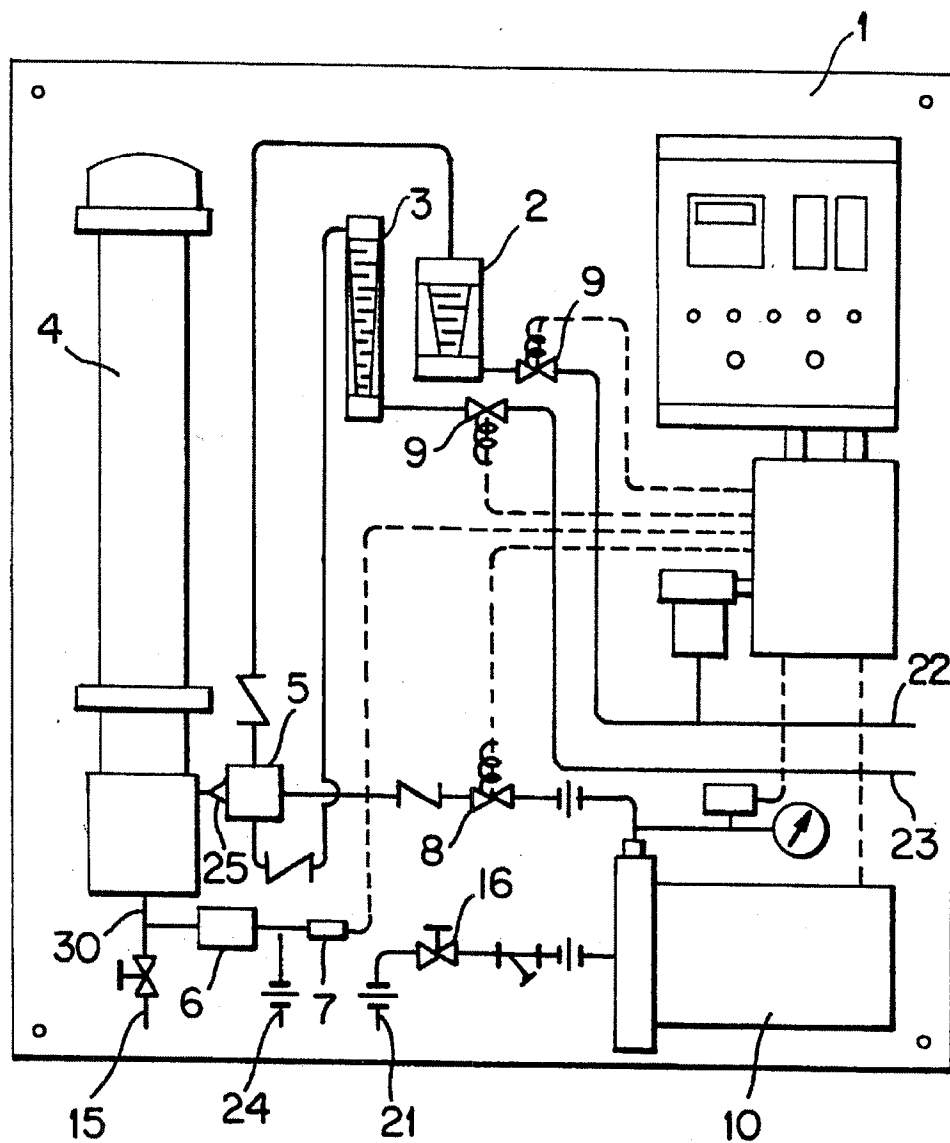


FIG. 1

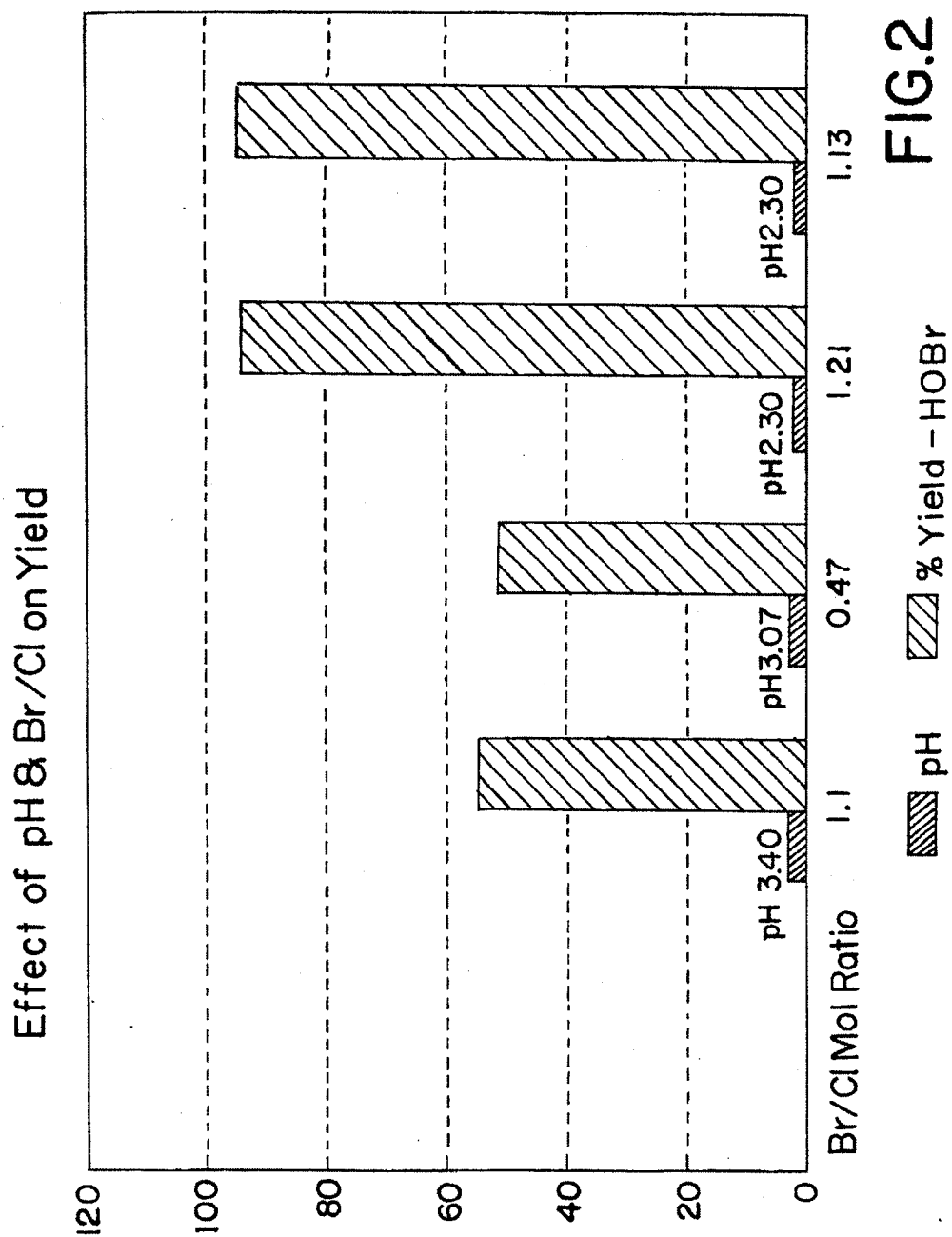


FIG.2

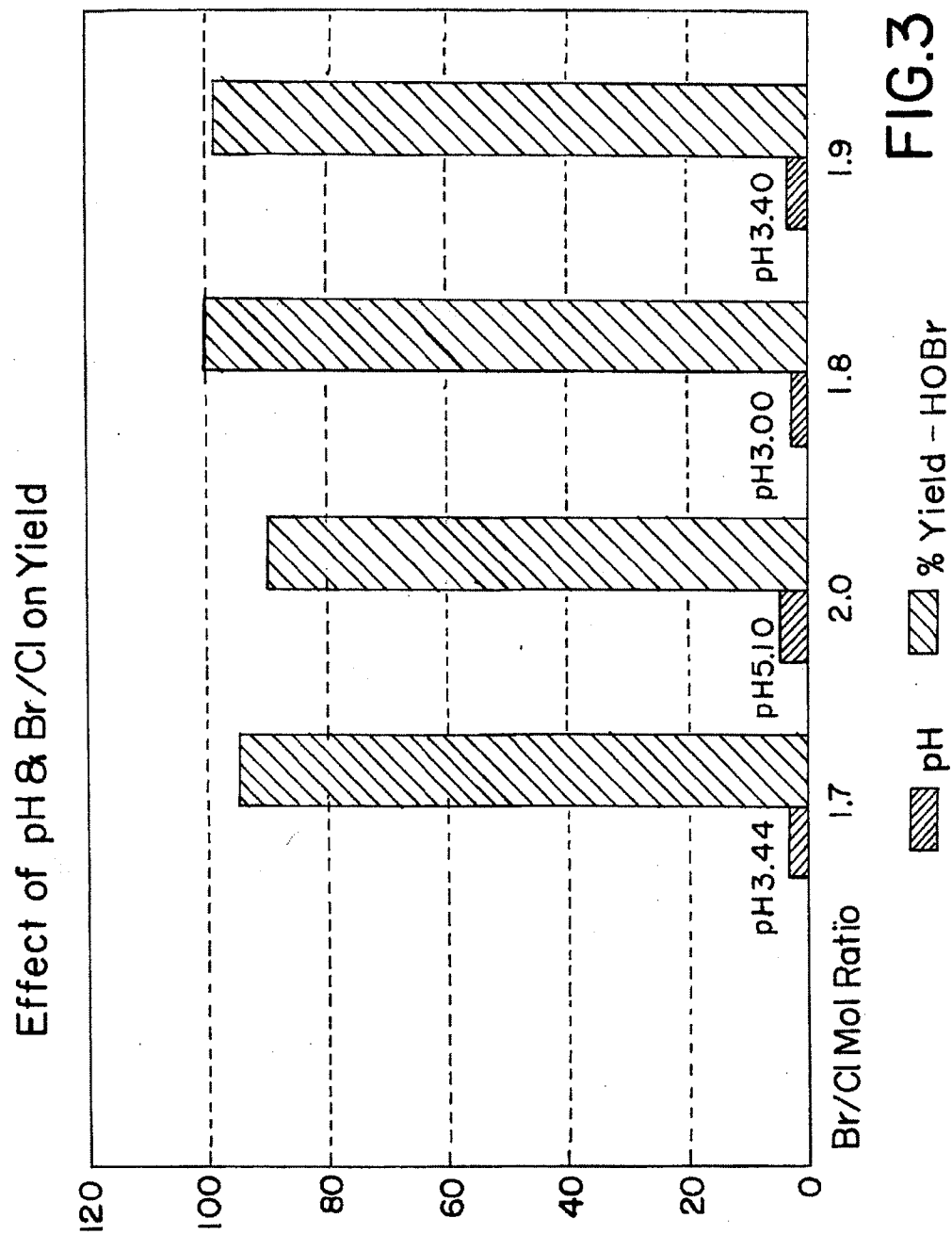


FIG. 3

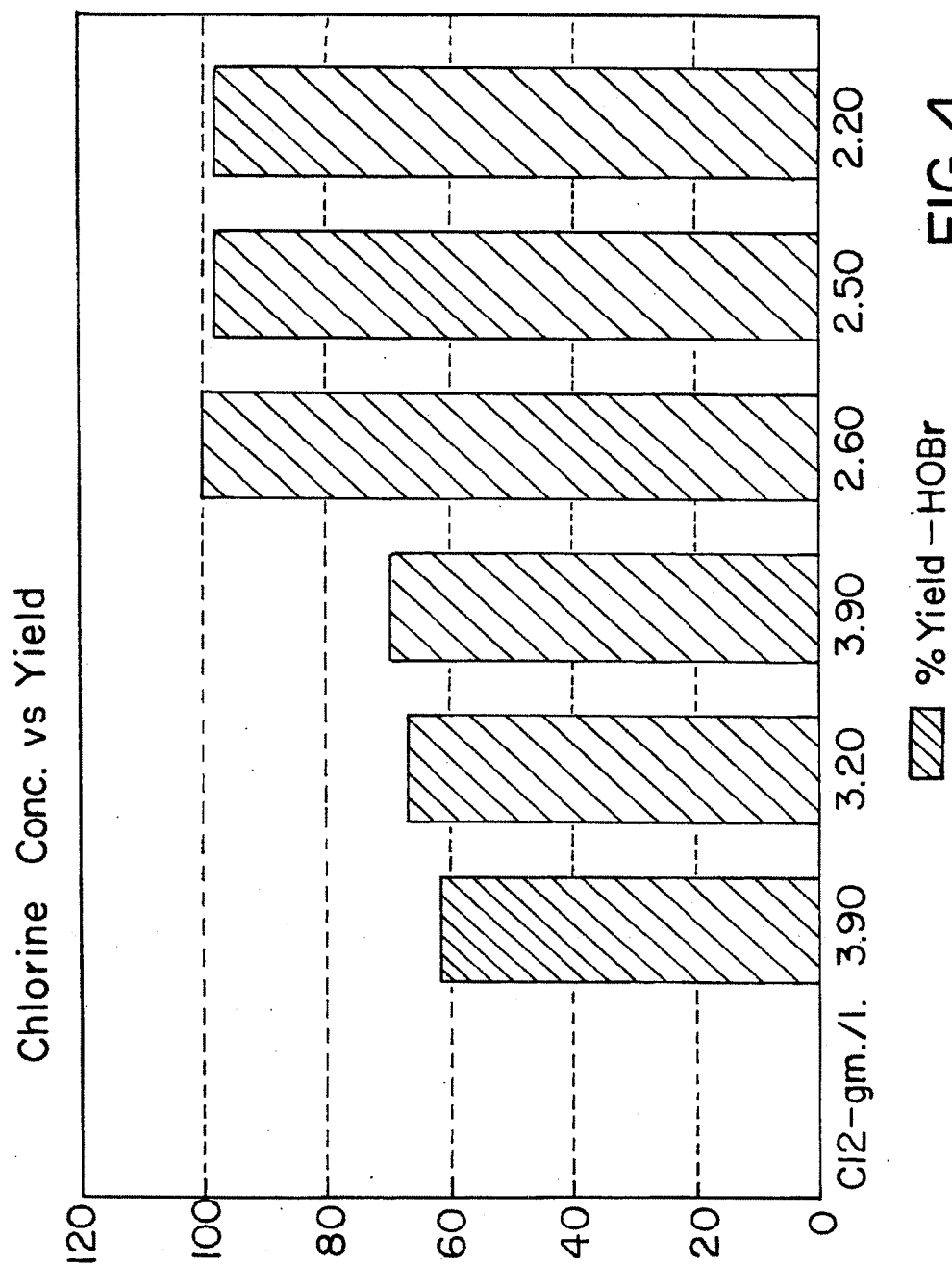


FIG. 4

# PROCESS FOR THE PREPARATION OF AQUEOUS SOLUTIONS OF BROMINE BASED DISINFECTANTS

This is a continuation of application Ser. No. 08/076,278, filed Jun. 11, 1993, now abandoned, entitled PROCESS FOR THE PREPARATION OF AQUEOUS SOLUTIONS OF BROMINE BASED DISINFECTANTS which is a continuation of Ser. No. 07/878,773 filed May 5, 1992, now abandoned.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to the production of concentrated aqueous solutions of bromine-based disinfectants. More particularly, the present invention relates to a process for the generation of hypobromous acid.

### 2. Description of the Prior Art

Industrial process waters, such as cooling tower water, paper plant water, and the like are often contaminated with undesirable microorganisms. Waste waters from sewage plants constitute another source of contaminants such as coliform, viruses, and other organisms which must be eliminated before discharge.

In cases where treated water is discharged into rivers and streams, it is important that low residual oxidant be maintained and that any disinfectant discharged be of low toxicity.

Chlorine has long been employed in the disinfection of drinking water, process water, cooling water, waste water, and the like. However, the use of chlorine has generated problems in some of the above uses. For example, the use of chlorine in the disinfection of drinking water containing organic contaminants has led to the formation of high levels of trihalomethanes, which are carcinogenic. The use of chlorine in process and cooling water has led to excessive corrosion of equipment. In addition, chlorine residuals in waste water lead to destruction of aquatic life when the waste water is discharged into streams or rivers.

Substitution of bromine-based disinfectants, such as hypobromous acid (HOBr), for chlorine has the following advantages:

- (i) hypobromous acid it is a more powerful disinfectant than chlorine, allowing the maintenance of much lower residuals to attain the same kill;
- (ii) hypobromous acid decomposes into harmless products much more rapidly than chlorine-based disinfectants such as hypochlorous acid, giving a much lower concentration of toxic materials at discharge into marine waterways;
- (iii) hypobromous acid is much less toxic to aquatic life (especially the initial species in the aquatic food chain) than the same concentration of hypochlorous acid;
- (iv) the ability to use lower residual concentrations of hypobromous acid, leads to lower concentrations of harmful by-products such as trihalomethanes; and
- (v) lower residual concentrations of hypobromous acid, plus its rapid rate of decomposition to non-toxic products, reduces the cost of total dehalogenation (before discharge) to insignificance.

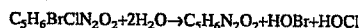
Several paths of decomposition of hypobromous acid are possible as shown in the following reactions:



There is much less corrosion with bromine-based disinfectants, such as hypobromous acid, than with chlorine. This is true for two reasons. First, the residual concentration of hypobromous acid is much lower than chlorine due to its higher potency against organisms and its rapid decomposition rate. Secondly, it has a lower oxidation potential than chlorine which has 2-3 times more corrosive effect than bromine-based disinfectants.

Various methods have been employed to introduce bromine-based disinfectant systems into aqueous solutions for the purpose of preventing the growth of harmful and offensive microorganisms.

Among these are various N-brominated organic compounds, in which the bromine atom is loosely bound and capable of rapid reaction to give hypobromous acid when added to water. An example of this type of compound is bromochlorodimethylhydantoin (BCDMH) which, when added to water, undergoes hydrolysis to give hypobromous acid and hypochlorous acid by the following reaction:



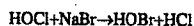
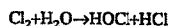
The hypohalous acids (HOBr and HOCl) thus generated are powerful disinfectants and will kill any organisms present and prevent the growth of any objectionable microbiological life forms. However, this type of brominated organic compound has several disadvantages. The cost is very high and a dimethylhydantoin by-product is produced. The presence of hypochlorous acid in the solution poses problems on discharge into streams or rivers due to its stability and toxicity to marine life.

Another method of generating hypobromous acid is by the hydrolysis of bromine chloride (BrCl) according to the following reaction:



Bromine chloride is a liquid under pressure. When used in the same type of cylinders used for chlorine, it requires a specially designed, expensive liquid feeder to proportion the bromine chloride into water. It also creates safety concerns due to the necessity of storing large quantities of gas on-site.

Yet another method of generating hypobromous acid is to chlorinate water and then to pump a solution of sodium bromide (NaBr) into water containing hypochlorous acid (HOCl). The following equations illustrate this method:



The disadvantage in using this method is that the water contacts chlorine before the hypobromous acid is formed and chlorinated by-products may be formed in waste the water. Also, in high chlorine demand water, the chlorine may not be available to oxidize the bromide ion ( $\text{Br}^-$ ) to hypobromite ion ( $\text{OBr}^-$ ) due to prior reaction. In addition, there is no control of reaction conditions to assure optimum conversion of the bromide to hypobromous acid. The concentration, pH and bromide/chlorine ( $\text{Br}/\text{Cl}$ ) mole ratio are all important in the above reactions. It is almost impossible to control all of these variables using a pump to add the bromide ion to the chlorinated water.

U.S. Pat. No. 4,451,376 (to J. D. Sharp) indicates that it is not efficient to prepare hypobromous acid directly in a biologically contaminated water system due to the loss of

hypochlorous acid and the resulting poor conversion of bromide ion to hypobromous acid. It also points out that the hypobromous acid should be prepared as a treating solution which then contacts the unwanted microorganism. It further points out the fact that if sodium hypochlorite or chlorine is combined with a bromide salt in a mixing tank in an effort to produce hypobromous acid, the hypobromous acid is not stable at concentrated levels and decomposes to bromine, bromate and bromite.

Thus, there is no method for generating hypobromous acid wherein all of the variables can be controlled by a single apparatus and where the yield of hypobromous acid approaches 100%.

Accordingly, it is an object of the present invention to provide novel processes for the generation of relatively concentrated solutions of hypobromous acid. Another object of the present invention is to provide a process which gives high yields of relatively concentrated hypobromous acid in water from non-hazardous reactants.

These and other objects, as well as the scope, nature and utilization of the invention will become apparent to those skilled in the art from the following description, the drawing, and the appended claims.

### SUMMARY OF THE INVENTION

The above problem is eliminated by the present processes. In the preferred process the compounds separately react in a relatively dilute water stream. In an alternate process the compounds are prereacted and the reaction mixture is introduced into the water stream. Preferably, the processes are carried out in an apparatus, hereafter referred to as a generator, which has an eductor. The residence time in the generator is very low. About 2000 ppm hypobromous acid are produced, which is subsequently diluted to use levels of about 0.1 to 3 ppm. The synthesis is completed under optimum conditions within seconds and the resulting hypobromous acid is further diluted immediately, thus minimizing decomposition reactions. In the process of U.S. Pat. No. 4,451,376, it is necessary to add a dispersing agent to the bromide salt before mixing with the chlorine donor to prevent these unwanted decomposition reactions in the concentrated hypobromous acid.

The preferred process for the preparing an aqueous solution of hypobromous acid comprises the steps of:

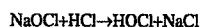
- (a) separately feeding compounds, which when reacted together yield hypobromous acid, via separate feed lines into a water stream, followed by complete mixing of the compounds;
- (b) allowing the compounds to react in the water stream to yield hypobromous acid and thereby form the aqueous hypobromous acid solution; and;
- (c) monitoring the pH of the formed aqueous hypobromous acid solution using a pH meter provided downstream of the reaction between the compounds which yield the hypobromous acid.

In one embodiment of this preferred process, the compounds which are separately fed into the water stream are gaseous chlorine and an aqueous solution of an alkali metal bromide or an alkaline earth metal bromide.

In the second embodiment of the preferred process, the compounds are also gaseous chlorine and an alkali metal bromide or an alkaline earth metal bromide. In this embodiment the chlorine gas is pumped into the water stream first and then the aqueous solution of the alkali metal or alkaline earth bromide is pumped into the hypochlorous acid solution resulting from the reaction of the chlorine and water.

An apparatus capable of carrying out the above embodiments is marketed by International Dioxide, Inc. under the trademark of OXYCHLOR II™ and is described in U.S. Pat. No. 5,009,875 (issued Apr. 23, 1991 to J. M. Kelley et al.), the disclosure of which is incorporated herein by reference. One skilled in the art would recognize that the apparatus described in the '875 patent can be modified to allow the water to be chlorinated first.

In a third embodiment of the preferred process, an aqueous mixture of alkali metal hypochlorite (e.g., sodium hypochlorite) and an acid (preferably hydrochloric acid) are substituted for the chlorine gas. This is done when it is desired to eliminate the storage of chlorine gas. In this embodiment the sodium hypochlorite (NaOCl) and hydrochloric acid (HCl) are premixed, before addition to the water stream, to give hypochlorous acid according to the following equation:



An excess of the acid may be added to the water solution to maintain the pH at the optimum level.

An apparatus capable of carrying out the above embodiment is the OXYCHLOR III™ generator marketed by International Dioxide, Inc.

An alternate process for preparing an aqueous solution of hypobromous acid comprises the steps of:

- (a) prereacting compounds which when reacted together yield hypobromous acid;
- (b) feeding the reaction mixture into a water stream to form the aqueous hypobromous acid solution; and
- (c) monitoring the pH of the hypobromous acid solution formed using a pH meter provided downstream of where the reaction between the compounds which form the hypobromous acid occurs.

The compounds used in the above process are gaseous chlorine and an alkali metal bromide or an alkaline earth metal bromide. The preferred alkali metal bromide is sodium bromide. Preferably the reaction mixture is fed into an eductor through which the water stream flows.

One skilled in the art will recognize that the apparatus described in the '875 patent can be repiped to allow the compounds to prereact before introduction into the water stream.

Optionally, a purge cycle may be included in the above processes in order to flush out any residual chemicals with water when the apparatus is shut down.

The aqueous hypobromous acid solution resulting from this process is added to the stream of water to be disinfected at a rate sufficient to give the desired final concentration of hypobromous acid in the water to be treated, usually in the range of 0.1 to 3 ppm.

### DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically depicts an apparatus useful in the practice of the present invention. The apparatus described is useful without modification for the first embodiment of the preferred process. It can be modified as previously discussed for use with the other embodiments and alternate process.

FIGS. 2-3 are bar charts to show the effect of pH & Br/Cl on yield.

FIG. 4 is a bar chart to show the chlorine concentration versus yield.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the preferred process of the present invention, compounds, which when reacted together produce hypobromous



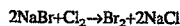
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acid, are fed via separate feed lines into a water stream, preferably into an eductor through which the water stream is flowing. In an alternate process, a reaction mixture containing the prereacted compounds is fed into a water stream, preferably into an eductor through which water stream is flowing.

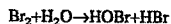
Preferred starting compounds are chlorine gas and a concentrated solution of an alkali metal bromide or alkaline earth metal bromide, preferably sodium bromide, dissolved in water. The highest possible concentration of sodium bromide in the aqueous solution is desirable because it allows the highest production of hypobromous acid. The sodium bromide concentration is preferably 40 weight % or greater, but concentrations of 20–40 wt. % are suitable. The chlorine gas is dissolved in and/or reacts with water to produce hypochlorous acid which reacts almost instantaneously with the bromide ion. The reactions which result in the formation of hypobromous acid are practically instantaneous and are as follows:



In general, it is preferable to dilute the compounds in a water stream rather than to allow pure chlorine gas to contact the sodium bromide solution because of the following side reaction between the sodium bromide and chlorine gas:



In this side reaction some of the bromide ion will be converted to free bromine. This is undesirable since the reaction of bromine with water is slower than the reaction of chlorine with water, although it will eventually give hypobromous acid by the following equation:



Alternatively, it is possible to use hydrochloric acid, sodium hypochlorite, and sodium bromide as reactants to achieve the same result without using gaseous chlorine.

In the preferred process, once the compounds are introduced into the water stream and diluted, they are mixed by passage through an in-line static mixer. Although the reactions leading to the formation of hypobromous acid are instantaneous, preferably a reaction chamber or line is provided so that sufficient time is provided for complete reaction to occur.

In the preferred process, shutoff valves are provided in the feed lines. When closed, the shutoff valves restrict any further flow of the compounds through the feed lines. In the apparatus marketed by International Dioxide, Inc., these shutoff valves can be actuated by a supply monitoring system if any one of the compounds is depleted, thus ceasing the generation of hypobromous acid and shutting the unit down.

The monitoring by the pH meter is extremely important to the objectives of this invention. The use of this pH meter permits the generation of hypobromous acid at high conversion under optimal conditions. Incomplete reaction of the sodium bromide or free chlorine and the presence of sodium bromide or free chlorine in the product is extremely undesirable. The optimum pH for the hypobromous acid solution is from about 2.3–2.8. This pH will give high conversions of the sodium bromide to hypobromous acid. Control points on the pH meter can be set to shut off the flow of compounds or to signal an alarm when the pH is outside of the set limits.

Preferably, the feed lines are under vacuum. This is an added safety feature to prevent escape of the compounds during operation or shutdown.

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Turning now to the drawing of FIG. 1, there is schematically depicted an apparatus for use in the preferred process which utilizes chlorine gas and an aqueous solution of sodium bromide as the separately fed reactants. All of the reactants required for the process can be mounted on a panel 1, which panel can be wall mounted if desired. In the system depicted, a supply means for water can be connected to inlet means 21. The amount of water provided to the reaction area can be controlled by valve 16. The pressure of the normal water supply is generally around 40 to 60 psig, but this is not critical. Lower pressures can be used as a booster pump 10 will compensate therefore. The flow of water cannot only be controlled by supply valve 16, but also by solenoid valve 8.

Gaseous chlorine is provided, preferably under vacuum, by feed line 22, with the supply rate being adjusted by chlorine meter 2. The aqueous sodium bromide solution is supplied by feed line 23, with the supply rate being adjusted by meter 3. Both of the feed lines contain solenoid valves 9, which can control the flow of reactants through the feed line.

The aqueous sodium bromide solution and chlorine gas are fed by their respective feed lines, preferably under vacuum, into eductor 5, through which the water stream flows. The chemical reactants and the water are then passed through a static mixer 25 to insure complete mixing of the compounds and into reactor column 4, wherein the reaction of the chlorine gas and the sodium bromide to form hypobromous acid takes place. The reactor column 4 preferably provides sufficient retention time to provide high yields of hypobromous acid. The resultant hypobromous acid solution is then transferred via line 30 from the reactor column to exit 24, from which the hypobromous acid solution can be passed to a holding tank or to its ultimate end use, for example, the treatment of waste water discharge in a sewage plant. Before exiting, however, the hypobromous acid solution can be viewed through sight glass 6. The hypobromous acid solution is also monitored by pH meter 7. The optimal pH of the product solution is between 2.3 and 2.8. A pH within this range indicates the generation process is proceeding at the optimum level. If a further analysis is to be performed, the hypobromous acid solution can be drawn from tap 15 provided at the base of reactor column 4.

The preferred source of bromide ion for use in this process and apparatus is an aqueous solution of sodium bromide; however, other water soluble, bromide-containing compounds can be used. Such compounds include alkali metal bromides, alkaline earth bromides, and hydrogen bromide (HBr).

The preferred source for generating the hypochlorous acid is chlorine gas, which reacts with water almost instantaneously to form the desired hypochlorous acid. Alternately, hypochlorous acid may be formed by acidification of a sodium hypochlorite solution (i.e., a bleach solution) in cases where it is desired not to store or use chlorine gas.

Based on the data from experimental runs made in an OXYCHLOR II™ generator, which data is presented below, certain process parameters are critical in producing high yields of hypobromous acid. Among these are concentration of chlorine when using concentrated aqueous sodium bromide solutions, pH of the generator effluent, and the bromide/chlorine (Br/Cl) mole ratio.

The concentration of chlorine (grams per liter) when mixed with a concentrated bromide solution, appears to be critical to the yields obtained in the above-described generator. For example, when a small (3.2 gallons per minute) nozzle was used in the water ejector system of the OXYCHLOR II™ generator, the yields of hypobromous acid were only in the 65% range. However, by simply increasing

the ejector size to give a flow of 5.2 gallons per minute water, with all other conditions being the same, the yield of hypobromous acid was increased to substantially 100%. This would equate to the requirement that the chlorine concentration be below 3 grams per liter when feeding a 40% sodium bromide solution to attain high yields of hypobromous acid.

The pH of the solution in which the hypobromous acid is being generated is also an important variable. Results have shown that a pH range of about 2.3 to 2.8 will, in general, give the highest yields of hypobromous acid from the generator when the bromide/chlorine mole ratio is near 1.0 or less.

The bromide/chlorine mole ratio is also important. At pH values above about 3.0 it has been observed that as this mole ratio approaches an optimum value of 1.5 or greater, the yield of hypobromous acid approaches 100%.

The chemistry of this process is not simple and there are side reactions which can be important in the efficiency of the hypobromous acid generation. For example, it was observed during the experimental runs that rather pronounced reddish-brown solutions resulted when the generator was operated at pH values above about 2.8. As the pH was decreased to below about 2.8 and approached 2.3, the color of the solution decreased markedly and approached a pale yellow color. The main reactions believed to occur in this generator are reactions (1) and (2) discussed previously.

Reaction (3), shown below, can produce some free bromine since, under the conditions of generator operation, free chlorine can occur in the water solution below pH 4.0 and can lead to the formation of free bromine.

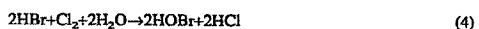


In turn, the free bromine can react with water to slowly form hypobromous acid according to the following equation:



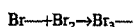
This reaction is rather slow when compared to the reaction rate of chlorine with water. The equilibrium constant for the above reaction is  $5.8 \times 10^{-9}$  at 25° C.

Also, the co-product hydrogen bromide (HBr) can react with hypochlorous acid to give additional hypobromous acid as shown in Reaction (4).

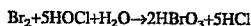


Thus, through various side reactions, the apparent yield of hypobromous acid could appear to be over 100%.

Reaction of free bromine ( $\text{Br}_2$ ) with a bromide ion ( $\text{Br}^-$ ) can form a perbromide ion ( $\text{Br}_3^-$ ) by the following reaction:



This complex ion has a deep red color. However, in the presence of excess hypochlorous acid, it probably reacts to give hypobromous acid and bromine, explaining the disappearance of the reddish-brown color. Another reason for the disappearance of the reddish-brown color is the fact that free bromine can react with hypochlorous acid by the following reaction:



The following examples will illustrate the invention but not limit the scope of the invention.

## EXAMPLES 1-11

These experiments were run in a generator manufactured by International Dioxide, Inc. without modification of the generator. In these experiments a 25% by weight aqueous solution of sodium bromide was fed through the sodium chlorite rotameter and the chlorine gas was fed through its regular feed line and the rotameter. The pH probe was standardized at pH 4.0 and 10.0 with standard buffer solution.

The total oxidant concentration was measured by the standard potassium iodide—thiosulfate method using a 10 ml. sample from the generator. The results are reported as ml. of thiosulfate used to react with the liberated iodine. These figures were then used to calculate the hypobromous acid content from the generator, not correcting for side reactions or excess hypochlorous acid. The ppm of hypobromous acid of by material balance has been calculated by assuming that the lowest number of moles of chlorine or sodium bromide fed to the generator gave 100% conversion to hypobromous acid. Because of the color changes observed during the various experiments, absorbance at 390 nanometers was measured.

The data gathered in these experiments is shown in Table I.

## EXAMPLES 12-21

These experiments were carried out exactly as indicated in Examples 1-11 except that a 20% by weight aqueous solution of sodium bromide was used instead of the 25% solution. The results of these runs are given in Table II.

## EXAMPLES 22-39

These experiments were carried out exactly as indicated in Examples 1-11 except that a 40% by weight aqueous solution of sodium bromide was used and a #13 (3.2 gallons per minute) or a #15 (5.2 gallons per minute) nozzle was used in the experiments. The results of these runs are given in Table III.

Analysis of these results have been plotted in FIGS. 2-4. The results indicate that when the bromide to chlorine mole ratios approach 1.0, a pH in the range of 2.3- 2.8 is necessary to get high conversions of sodium bromide to hypobromous acid. They also indicate that a bromide to chlorine mole ratio of 1.5 tends to give higher conversions to hypobromous acid, other conditions such as pH being constant. Thirdly, they show that there is a critical concentration of chlorine—that chlorine concentrations above about 3.0 grams per liter reduced the yield of hypobromous acid when concentrated sodium bromide solutions (40% by weight) were fed.

## EXAMPLE 40

An Oxychlor III™ generator manufactured by International Dioxide, Inc. is used in this experiment. The major difference between this reaction and the reaction carried out in the Oxychlor II™ generator used in Examples 1- 39 is that the chlorine is generated by reacting hydrochloric acid and sodium hypochlorite (bleach). Two separate streams of hydrochloric acid and bleach are mixed prior to entering the #15 eductor and then mixing with the water. The sodium bromide rotameter is set at 30 to give a flow of 138.2 lbs./day of pure sodium bromide. The sodium hypochlorite rotameter is set to deliver 63 lbs/day of pure sodium hypochlorite (504 lbs/day of 12.5 wt % commercial bleach). The hydrochloric

acid rotameter is adjusted to give the solution in the generator a pH of about 3.0. The water exiting the generator should contain about 775 ppm of hypobromous acid, which is substantially 100% yield based on the bleach fed to the generator.

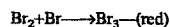
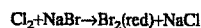
## EXAMPLE 41

An Oxychlor II™ generator equipped with a #15 nozzle is modified to allow the water to be chlorinated first and a concentrated 40% sodium bromide solution is pumped into the water stream downstream from the chlorinator. The chlorinator rotameter is set for about 60 lbs. of chlorine gas per day. The chemical feed pump is set to deliver 138 lbs. per day of pure sodium bromide. After sufficient time is elapsed to allow for equilibrium, a sample should be taken from the generator and analyzed for hypobromous acid content. The yield of hypobromous acid should be 98%.

## EXAMPLE 42

An Oxychlor II™ unit is repiped to allow the pure chlorine gas and a 40% sodium bromide solution to prereact before dilution with water in the eductor system. Although

some hypobromous acid should be produced immediately upon start-up, the solution will be considerably redder in color than when the components are fed separately into the eductor and thus diluted while reacting. The red color is probably due to the following reactions:



While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

TABLE I

## HYPOBROMOUS ACID RUNS AT 25 WT. % AQUEOUS SODIUM BROMIDE

Ex. #	Cl <sub>2</sub> lbs/day	25% NaBr lbs/hr	NaBr (pure) lbs/day	NaBr lb-moles/day	Cl <sub>2</sub> lb-moles/day	pH	Dilution With Water Before Measurement of Absorption at 390 nm	Absorption 390 nm	ml Thio-sulfate (10 ml Sample)	ppm HOBr (Analytical)	ppm HOBr (Material Balance)	Theoretical HOBr lbs/day	HOBr % Yield
1	28	0	0	0	0.39	3.17	0	0	0.50	170 (Cl <sub>2</sub> )	—	0	—
2	35	4.0	24.0	0.23	0.49	3.07	0	0.249	0.90	429	835	22.6	51.3
3	50	14.0	84.0	0.82	0.70	3.36	1/1	0.813	2.90	1384	2528	68.3	54.9
4	60	20.6	123.6	1.20	0.84	4.04	1/5	0.500	3.95	1885	3012	81.4	62.6
5	Low	0	0	0	Low	2.90	—	—	0.85	290 (Cl <sub>2</sub> )	—	0	—
6	40	16.0	96.0	0.93	0.56	2.75	1/10	0.089	2.45	1169	1188	54.2	98.4
7	48	16.0	96.0	0.93	0.67	5.03	1/10	0.098	1.67	797	1422	64.9	56.0
8	55	16.0	96.0	0.93	0.77	2.30	1/10	0.007	3.25	1551	1645	75.1	94.2
9	—N.R.	27.5	165.0	1.60	—	2.60	1/10	0.131	3.85	1838	1825	(83.3)	100.7
10	—N.R.	37.4	224.4	2.18	—	2.60	1/10	0.201	4.90	2338	2338	(106.7)	100.0
11	100	27.5	165.0	1.60	1.41	2.30	1/10	0.043	5.91	2821	2993	136.6	94.2

Experiments 1-4 - Oxychlor Basic w/pH Meter; 2.25 Gal/Min #16 Nozzle; 150 PPD Small Rotameter

Experiments 5-11 Oxychlor II w/pH meter; Gal/Min #13 Nozzle; Large Rotameter

N.R. means not reported

TABLE II

## HYPOBROMOUS ACID RUNS AT 20 WT. % SODIUM BROMIDE

Ex. #	Cl <sub>2</sub> lbs/day	20% NaBr lbs/hr	NaBr (pure) lbs/day	NaBr lb-moles/day	Cl <sub>2</sub> lb-moles/day	pH	Dilution With Water Before Measurement of Absorption at 390 nm	Absorption 390 nm	ml Thio-sulfate (10 ml Sample)	ppm HOBr (Analytical)	ppm HOBr (Material Balance)	Theoretical HOBr lbs/day	Yield % HOBr
12	15	7.2	34.5	0.33	0.21	5.16	0	0.533	0.83	395	472	20.4	83.6
13	20	7.2	34.5	0.33	0.28	3.45	0	0.611	1.00	477	631	27.3	75.6
14	30	7.2	34.5	0.33	0.42	2.45	0	0.295	1.66	792	751	32.5	105.0
15	28	18.0	86.2	0.84	0.39	5.59	1/10	0.116	1.37	653	883	38.2	63.7
16	32	18.0	86.2	0.84	0.45	3.45	1/10	0.090	1.69	806	1009	43.6	79.8
17	45	18.0	86.2	0.84	0.63	2.68	0	0.684	2.25	1073	1419	61.3	75.6
18	45	30.0	143.7	1.40	0.63	5.36	1/10	0.172	2.34	112	1419	61.3	78.6
19	55	30.0	143.7	1.40	0.77	3.24	1/10	0.187	2.93	1398	1736	75.0	80.4
20	75	30.0	143.7	1.40	1.06	2.46	1/10	0.134	4.42	2108	2368	102.3	89.0
21	15	30.0	143.7	1.40	0.20	6.41	1/10	0.048	0.88	419	448	19.4	93.5

Eductor = 43,200 lbs water/day

TABLE III

HYPOBROMOUS ACID RUNS AT 40 WT. % AQUEOUS SODIUM BROMIDE													
Ex. #	Cl <sub>2</sub> /# lbs/day	40% NaBr lbs/hr	NaBr (pure) lbs/day	NaBr lb-moles/day	Cl <sub>2</sub> moles/day	pH	Dilution With Water Before Measurement of Absorption at 390 nm	Absorption 390 nm	ml Thio-sulfate (10 ml Sample)	ppm HOBr (Analytical)	ppm HOBr (Material Balance)	Theoretical HOBr lbs/day	Yield % HOBr
#13 Nozzle													
22	100	14.4	138.2	1.34	1.43	2.59	1/10	0.065	6.22	2966	3013	130.2	98.4
23	53	14.4	138.2	1.34	0.75	3.44	1/10	0.197	3.27	1559	1682	72.7	95.1
24	47	14.4	138.2	1.34	0.66	5.05	1/10	0.191	2.80	1335	1480	63.9	90.2
25	100	27.7	265.9	2.58	1.43	3.03	1/10	0.437	6.71	3200	3185	137.6	100.4
26	96	27.7	265.9	2.58	1.35	3.43	1/10	0.436	6.27	2990	3041	130.8	98.3
27	86	27.7	265.9	2.58	1.21	5.05	1/10	0.416	5.62	2680	2715	117.3	98.7
28	150	27.7	265.9	2.58	2.10	2.58	1/10	0.172	6.22	2966	4810	203.5	61.6
29	125	27.7	265.9	2.58	1.76	2.77	1/10	0.239	5.65	2695	4030	170.5	66.8
30	125	18.8	181.0	1.76	1.76	2.18	1/10	0.085	5.77	2752	3946	170.5	69.7
31	150	23.3	224.2	2.18	2.11	2.18	1/10	0.126	6.71	3200	4722	204.5	67.8
#15 Nozzle													
32	125	27.7	265.9	2.58	1.76	2.56	1/10	0.241	5.85	2790	2730	170.5	102.1
33	150	27.7	265.9	2.58	2.11	2.44	1/10	0.175	6.64	3167	3275	204.5	96.7
34	150	23.3	224.2	2.18	2.11	2.30	1/10	0.145	6.04	2881	3275	204.5	87.9
#14 Nozzle													
35	150	27.7	265.9	2.58	2.11	2.52	1/10	0.036	3.96	1889	2156	204.5	87.6
36	60	14.4	138.2	1.34	0.84	3.29	1/10	0.083	1.63	777	775	81.9	100.3
37	150	18.8	181.0	1.76	2.11	2.57	1/10	0.018	3.58	1707	1613	170.5	105.8
38	60	14.4	138.2	1.34	0.84	3.43	1/10	0.075	1.60	763	743	78.5	102.7
39	125	14.4	138.2	1.34	1.76	2.69	1/10	0.008	2.69	1283	1182	124.9	108.5

#13 Nozzle = 3.2 gals/min or 43,200 lbs of water/day

#14 Nozzle = 8.8 gal/min or 105,684 lbs water/day

#15 Nozzle = 5.2 gal/min or 62,449 lbs of water/day

What is claimed is:

1. A process for preparing an aqueous solution of hypobromous acid, which comprises the steps of:

- flowing a water stream through an eductor to create a vacuum;
- separately and simultaneously drawing into the eductor by said vacuum and then into the water stream, via separate feed lines, (i) gaseous chlorine and (ii) an aqueous solution of an alkali metal bromide or an alkaline earth metal bromide having a concentration of at least 20% by weight of the bromide, wherein the amounts of the gaseous chlorine and the bromide are sufficient to maintain a pH of about 2 to about 6.4 in the resulting aqueous hypobromous acid solution, and with the bromide to chlorine mol ratio being between about 0.5 and 2.0;
- immediately mixing and reacting the chlorine, the bromide, and the water by passage through an in-line mixer;
- completing the reaction in a reaction chamber or line; and
- recovering from said reaction chamber or line said aqueous solution of hypobromous acid having a pH of about 2 to about 6.4, in which the yield of hypobromous acid is at least about 51%.

2. The process of claim 1, further comprising the step of monitoring the pH of the aqueous solution of hypobromous acid formed using a pH meter provided downstream of where the reaction between the gaseous chlorine and the bromide which form the hypobromous acid occurs.

3. The process of claim 1, wherein the alkali metal bromide is sodium bromide.

4. The process of claim 3, wherein the aqueous sodium bromide feed solution has a concentration of about 40% by

weight or greater and wherein the amount of gaseous chlorine in the water stream is no greater than 3000 milligrams per liter.

5. The process of claim 3, wherein the bromide to chlorine mole ratio is less than about 1.5 to 1 and the pH is about 2.3 to 2.8.

6. The process of claim 3, wherein the ratio of bromide to chlorine is above about 1.5 and the pH is above about 3.

7. The process of claim 2, further comprising the step of purging the eductor with water after the chlorine, the bromide, and the water react to form the aqueous solution of the hypobromous acid.

8. The product prepared by the process of claim 3, wherein the hypobromous acid solution has a concentration of about 750-3000 ppm of hypobromous acid.

9. The process of claim 1, wherein the pH is about 3 and wherein the bromide/chlorine mole ratio is about 1.5 or greater.

10. The process of claim 1, wherein the bromide/chlorine mole ratio is about 1 or less and wherein the pH is between about 2.3 and 2.8.

11. The process of claim 9, wherein the alkali metal bromide is sodium bromide.

12. The process of claim 11, wherein the sodium bromide concentration is about 20 to about 40% by weight.

13. The process of claim 11, wherein the aqueous sodium bromide feed concentration is about 40% by weight and the amount of gaseous chlorine in the water stream is below about 3000 milligrams per liter.

14. The process of claim 1, wherein the mixer is a static mixer.

15. The process of claim 1, wherein the aqueous bromide solution has a concentration of about 40% by weight and the chlorine concentration in the water stream is below about 3 grams per liter.

## 13

16. The process of claim 15, wherein the chlorine concentration is 2.6 grams per liter or less and wherein the yield of hypobromous acid is about 98-100%.

17. A process for preparing an aqueous solution of hypobromous acid, which comprises the steps of:

(a) flowing a water stream through an eductor to create a vacuum;

(b) separately and simultaneously drawing into the eductor by said vacuum and then into the water stream, via separate feed lines, (i) an aqueous mixture of an alkali metal hypochlorite and an acid which react to produce hypochlorous acid and (ii) an aqueous solution of an alkali metal bromide or an alkaline earth metal bromide having a bromide concentration of at least 20% by weight, wherein the hypochlorite, the acid, and the bromide are fed in amounts sufficient to maintain a pH of about 2 to about 6.4 in the resulting aqueous hypobromous acid solution;

## 14

(c) immediately mixing and reacting the hypochlorous acid, the bromide, and the water by passage through an in-line mixer;

(d) completing the reaction in a reaction chamber or line; and

(e) recovering from said reaction chamber or line said aqueous solution of hypobromous acid having a pH of about 2 to about 6.4, in which the yield of hypobromous acid is at least about 51%.

18. The process of claim 17, wherein the alkali metal hypochlorite is sodium hypochlorite, the acid is hydrochloric acid, and the alkali metal bromide is sodium bromide.

19. The process of claim 18, wherein the sodium bromide is an aqueous solution having concentration of at least about 40%, by weight, or greater.

\* \* \* \* \*

# APPENDIX

## F

1

3,316,173

## PROCESS FOR TREATING WATER WITH BROMINE

Jack F. Mills, Robert D. Goodenough, and William F. Nekervis, all of Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Continuation of application Ser. No. 283,596, May 27, 1963. This application June 1, 1966, Ser. No. 537,246

5 Claims. (Cl. 210-62)

This application is a continuation of Ser. No. 283,596, filed May 27, 1963, now abandoned.

This invention relates to a process for treating an aqueous solution with bromine to control the microorganisms therein. More particularly, it relates to a process for treating water with elemental bromine obtained from the polybromide form of an anion exchange resin.

The use of chlorine and bromine in the disinfection and sterilization of water supplies for many diverse purposes is well known. Chlorination of municipal water supplies has been a standard practice in the United States and abroad for many years. Addition of bromine in concentrations up to 5 parts per million (p.p.m.) to sanitize water was described by Henderson in United States Patent 1,995,639. Now it is generally recognized that on an equimolar basis, bromine is several times more effective than chlorine for the control of bacteria, algae, slime, and other microorganisms in water supplies. In fact, excellent control of many bacteria in water can be effected using as little as 0.1 p.p.m. bromine.

With badly contaminated water, a heavy initial shock treatment with from 3 to 30 p.p.m. bromine may be desirable to kill the contaminating microorganisms after which a residual bromine concentration of 0.1 to 1.0 p.p.m. is generally effective in maintaining sanitary water. The level of the shock treatment is, of course, dependent on the nature of the contaminating microorganisms. For treatment of potable water, shock treatment with 3 to 5 p.p.m. bromine generally suffices to kill the undesired bacteria. However, heavy contamination with slime and algae, as may be encountered in water used in industrial cooling towers, often requires shock treatment with 10 to 30 p.p.m. of bromine. For example, while treatment with 2 p.p.m. bromine noticeably inhibits the growth of *Chlorella*, a common strain of algae, 10 p.p.m. bromine are required for pronounced inhibition and between 10-20 p.p.m. for complete kill.

In addition to its effectiveness as an antimicrobial, there are further advantages to the use of bromine in sanitizing water supplies. Because of its lower volatility, maintaining a desired residual level of halogen in the treated water is easier with bromine than chlorine, particularly under conditions of turbulent flow and agitation. Furthermore, bromine imparts little or no undesirable taste or odor to the treated water. Indeed, since bromine acts to destroy suspended or dissolved organic matter which often causes undesirable color and odor, it is particularly suited for use as a sanitizing agent for swimming pools where sparkling clear, colorless and odorless water is highly desirable.

Thus, treating water with bromine is advantageous in providing large volumes of water suitable as potable municipally supplies and for many other commercial, industrial and residential purposes. In particular, bromine is extremely desirable for use as a sanitizing agent for swimming pools, industrial cooling towers, and similar recirculating water systems since a very low concentration of bromine is effective both in destroying the bacteria initially present and in maintaining hygienic conditions in spite of repeated recontamination.

2

However, because of the highly corrosive nature of elemental bromine, a serious hazard is involved in its use. The danger in handling liquid bromine has discouraged its use as a sanitizing agent, particularly in smaller systems where elaborate equipment for handling liquid bromine is not feasible. In some localities use of liquid bromine has been restricted by ordinance.

Thus, there exists a need for a safe and practical process whereby bromine can be stored, handled, and added to water by unskilled personnel. Such a process requires a form of bromine which is easily and safely prepared, which is stable during storage and shipment, which does not cause serious burns in case of accidental skin contact, and yet which releases elemental bromine as required for sanitizing treatment.

It has now been discovered that the polybromide form of strongly basic, quaternary ammonium anion exchange resins is an extremely convenient, effective, and safe means for handling elemental bromine for use in treating water to control microorganisms. Essentially the polybromide resin serves as a reservoir from which elemental bromine can be removed as required to establish or to maintain control of bacteria, algae, slime, and other microorganisms in a body of water. Not only do such polybromide resins possess highly useful and desired properties in respect to both bromine loading and elution characteristics, but also such polybromide resins are chemically stable for prolonged periods under normal storage conditions and can be prepared, stored, and shipped safely without degradation in quality. Although definitely not recommended, momentary accidental contact of the polybromide resin even with wet skin will not cause burns. Furthermore, the aqueous solution obtained by contact of the polybromide resin with water is sufficiently dilute so that burns will not result from brief skin contact.

Thus, the invention described herein concerns an improved process for treating water with bromine. More particularly, this improved process comprises: (1) contacting an anion exchange resin in polybromide form with water whereby bromine is removed from the polybromide resin to give an aqueous solution containing from 10 to 10,000 p.p.m. bromine and (2) mixing a sufficient amount of said aqueous bromine solution with the water to be treated to establish therein a concentration in the range from about 0.02 to 30.0 p.p.m. bromine.

The adsorption of elemental bromine by an anion exchange resin was reported in Chem. and Ind., 1238 (1957) by Aveston and Everest who found that when an anion exchange resin was treated with an aqueous solution containing elemental bromine, the polybromide anion,  $Br_n^-$  wherein  $n$  is 3, 5 or 7, became the predominant anionic species in the resin phase. With a quaternary ammonium resin and excess bromine, the resin was converted to the  $Br_7^-$  form by adsorption of 3 moles of bromine per equivalent of resin.

Ziegler in Angew. Chemie, 71, 283 (1959) reported that the polybromide resin was stable for a period at least 1.5 years. Furthermore, Ziegler found that the bromine was quantitatively eluted from the resin as bromide ion by treatment of the polybromide resin with an aqueous solution of a reducing agent, such as sulfur dioxide or sodium bisulfite. However, elution of bromine from the polybromide resin as an aqueous solution containing from 10 to 10,000 p.p.m. of elemental bromine as described herein has not been previously reported.

In the practice of the present invention, commercial anion exchange resins prepared by the reaction of a chloromethylated styrene-divinylbenzene resin with an appropriate organic amine are suitable as bromine carriers. Strongly basic, quaternary ammonium anion exchange resins of the type described by McBurney in

United States Patent 2,591,573 and by Bauman and McCellar in United States Patent 2,614,099 are particularly desirable. Weakly basic polyamine anion exchange resin, such as described by McBurney in United States Patent 2,591,574, may also be employed although the polyhalide form of these resins is not as stable.

Since the operating characteristics of the polybromide anion exchange resin column are similar to those of conventional ion exchange resin columns, commercial resins and conventional operating techniques are generally satisfactory in terms of such factors as degree of resin cross-linking, mesh size, flow rates, etc. While commercial anion exchange resins are commonly available in the chloride form, any anionic form may be employed so long as the anionic component is exchangeable by bromide or polybromide ions. Hydrolysis of bromine in the aqueous solution used to prepare the polybromide resin is generally sufficient to convert the resin to the desired bromide form. However, conversion from one anionic form to another is readily accomplished by well-known ion exchange techniques if necessary.

A particularly effective method for the preparation of a suitable polybromide resin is to pass an essentially saturated solution of bromine in aqueous sodium bromide slowly up through a bed of quaternary ammonium anion exchange resin. In this manner a commercial resin having a dry weight capacity of 3.50 meq./g.,  $\text{Cl}^-$  form, rapidly adsorbed 3 moles of bromine per equivalent of quaternary ammonium groups. The resulting polybromide resin in wet form contained about 48.6 weight percent bromine. This adsorbed bromine was quantitatively removed by treatment with a sodium bisulfite solution. An attempt to load the resin further under more forcing conditions resulted in bromination of the resin matrix, the elutable bromine content remaining at about 3 moles per equivalent of resin. A cubic foot of wet quaternary ammonium resin in the  $\text{Br}_7^-$  form contains about 40 pounds of bromine, an amount sufficient to treat a 25,000 gal. swimming pool for a normal period of at least 30 days.

If the polybromide resin is dried or exposed to large volumes of air, some of the adsorbed bromine is lost. However, if stored in a sealed container of bromine-resistant material such as polyvinyl chloride, the resin is stable for prolonged periods.

With conventional flow rates of from 1 to 10 g.p.m./ft.<sup>2</sup> of resin bed cross-sectional area, elution of bromine from the polybromide resin by passing water through the resin bed is essentially independent of the exact method of contact. An equilibrium is rapidly established between the bromine adsorbed by the anion exchange resin and that present in the aqueous phase. At room temperature the aqueous phase in contact with a quaternary ammonium resin in a fully loaded  $\text{Br}_7^-$  form contained about 7,000 p.p.m. bromine. Elution studies with a column of this resin indicated that the bromine concentration in the eluent dropped to about 1,300 p.p.m. after 100 bed volumes of water passed through the column. After passage of 1,400 bed volumes, the bromine concentration in the eluent dropped to about 50 p.p.m. and about 95 percent of the adsorbed bromine had been removed. Further elution reduced the residual bromine content of the resin still lower and the eluent bromine concentration then dropped to 10 p.p.m. and less.

Temperature does have a marked effect on the equilibrium of bromine between the resin and aqueous phases. For example, water in contact with an approximately equivalent amount of polybromide resin containing 2.14 moles of bromine per equivalent of resin had an equilibrium concentration of about 13,800 p.p.m. bromine at 55° C. and 4,270 p.p.m. at 27° C.

Regeneration of the exhausted or partially exhausted polybromide resin is readily achieved by treatment with a more concentrated bromine solution whenever desired, generally when the concentration of bromine in the eluent

falls below a given level. Yet obviously a higher eluent concentration of bromine is needed for a shock treatment requiring 10-30 p.p.m. bromine in the treated water than for maintaining a residual of 0.02-1.0 p.p.m. bromine. Hence, the frequency of regeneration will depend on the requirements of the particular system.

The bromine-containing eluent solution can be metered and added to another body of water as required to establish or to maintain a desired bromine concentration in the treated water. Conventional analytical techniques can be employed to determine bromine concentrations and to control the treatment process. If desired, automatic equipment can be used to monitor continually the bromine concentration in the treated water and to add the more concentrated bromine eluate as required to maintain the bromine concentration within desired limits. Such control is particularly suitable with a recirculating system such as commonly employed in residential swimming pools where a portion of the water circulating through the system can be diverted by suitable means to pass through and to elute bromine from a polybromide resin column.

The following examples illustrate further the invention described herein but are not to be construed as limiting its scope.

#### Example 1.—Polybromide resins

A. A portion of 20/50 mesh commercial quaternary ammonium styrene-divinylbenzene anion exchange resin having a dry weight capacity of 3.5 meq./g.  $\text{Cl}^-$  form (Dowex 1-X8 resin) was placed in a 1" I.D. glass column and loaded with bromine by slowly passing an excess of an aqueous solution containing about 35 wt. percent bromine and 17 wt. percent sodium bromide up through the column. After complete loading, the excess bromine solution was drained from the column and the polybromide resin rinsed with a small amount of water. A sample of the resulting wet polybromide resin was found to contain 48.6 wt. percent bromine. The adsorbed bromine was quantitatively removed by treatment of the resin with a sodium sulfite solution and corresponded to a theoretical capacity of 3 moles of bromine/equivalent of resin anion exchange capacity.

B. In an attempt to load the resin further, the concentrated aqueous bromine solution was warmed to 50° C. and recycled through the resin bed for several hours. The resin was then allowed to stand at room temperature for several days in contact with the bromine solution. The resulting wet resin was found to contain 64.9 wt. percent total bromine. However, after treating this resin with excess sodium sulfite solution, it retained 16.4 wt. percent bromine indicating bromination of the resin matrix. The elutable bromine was equivalent to about 3 moles of bromine per equivalent of initial resin capacity.

C. In a similar manner the polybromide forms of other styrene-divinylbenzene resin containing from 1 to 16% divinylbenzene were prepared. Also, a quaternary poly(vinylpyridine) resin as described by Greer in United States Patent 2,801,223 and a commercial quaternized polyethoxypolyamine resin were converted to similar polybromide forms. Although the bromine capacities of these resins were similar in proportion to their initial anion exchange capacity, the latter two resins were less stable than the preferred quaternary ammonium styrene-divinylbenzene resins.

#### Example 2.—Elution characteristics

Using a 1" I.D. column filled with the polybromide form of Dowex 1-X8 resin prepared as described in Example 1A, a series of elution runs was made at room temperature. No appreciable variation in elution characteristics was found using flow rates of 5 and 10 g.p.m./ft.<sup>2</sup>, a bed depth of 18 and 36 inches, and upflow and downflow feed. Table I presents data from a typical elution run



using a wet resin containing initially 48.5 wt. percent bromine.

TABLE I.—ELUTION CHARACTERISTICS

Bed Volumes of Eluent	10	50	100	300	600	1,400
Br <sub>2</sub> in eluent, p.p.m.	7,000	3,000	1,300	350	150	50
Total Br <sub>2</sub> eluted, percent	9.9	30.0	55.2	74.8	85.5	95.4

*Example 3.—Swimming pool unit*

A small resin column, 4" in diameter and 18" high, loaded with 0.13 ft.<sup>3</sup> of Dowex 1-X8 resin in the polybromide form and containing about 5.2 lbs. of bromine, was installed in the recycle line of a 20,000 gallon outdoor residential pool. By means of appropriate valves, a portion of the recycle water could be diverted after the filter unit to pass through the resin column, thereby eluting a portion of the adsorbed bromine for addition to the main recycle stream.

Initially flow of recycle water through the resin column was controlled manually to maintain a bromine concentration in the main body of the pool between about 0.70 and 1.20 p.p.m. Subsequently an automatic instrument was installed to measure the residual bromine in the recycle stream and to control a solenoid valve on the line to the polybromide column thereby diverting a portion of the recycle stream through the polybromide resin column intermittently as required to maintain a desired bromine concentration. For example, in a warm mid-afternoon period, the resin column was used with a cycle of about 10 minutes on-stream followed by about 20 minutes off-stream. After each on-stream period, the bromine concentration in the pool continued to rise for a few minutes because of the pool mixing characteristics before dropping slowly as the bromine was consumed. Nonetheless the bromine concentration in the pool was easily maintained between about 0.80 to 1.05 p.p.m. During the night, bromine consumption was essentially nil.

During an extended test period with the polybromide resin column, the swimming pool showed no signs of algae growth and maintained an essentially sterile condition with a bacterial plate count of less than 0.1 per cc.

We claim:

1. In a process for treating an aqueous solution with bromine, the improvement which comprises: passing the aqueous solution through a bed of a water-

insoluble anion exchange resin in polybromide form, whereby bromine is removed from the polybromide resin by the aqueous solution.

2. In a process for treating an aqueous solution with bromine to control the microorganisms therein, the improvement which comprises:

(1) contacting a water-insoluble anion exchange resin in polybromide form with an aqueous solution whereby bromine is removed from the polybromide resin to give an aqueous solution containing from 10 to 10,000 p.p.m. bromine and

(2) mixing a sufficient amount of said bromine solution with the aqueous solution to be treated to establish therein a concentration in the range from about 0.02 to 30.0 p.p.m. bromine.

3. The process of claim 2 wherein a portion of the aqueous solution to be treated is used to remove bromine from the polybromide resin.

4. The process of claim 2 wherein the water-insoluble anion exchange resin is a quaternary ammonium anion exchange resin.

5. The process of claim 4 wherein the predominate anionic species in the resin phase prior to initial elution is the polybromide anion, Br<sub>n</sub><sup>-</sup>, wherein n is an odd integer from 3 to 7 inclusive.

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# APPENDIX

## G



US005795487A

**United States Patent** [19]**Dallmier et al.**[11] **Patent Number:** **5,795,487**[45] **Date of Patent:** **\*Aug. 18, 1998**

[54] **PROCESS TO MANUFACTURE STABILIZED ALKALI OR ALKALINE EARTH METAL HYPOBROMITE AND USES THEREOF IN WATER TREATMENT TO CONTROL MICROBIAL FOULING**

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[75] **Inventors:** **Anthony W. Dallmier; William F. McCoy.** both of Naperville, Ill.

[73] **Assignee:** **Nalco Chemical Company,** Naperville, Ill.

[\*] **Notice:** The term of this patent shall not extend beyond the expiration date of Pat. No. 5,683,654.

[21] **Appl. No.:** **778,598**

[22] **Filed:** **Jan. 3, 1997**

[51] **Int. Cl.<sup>6</sup>** ..... **C02F 1/50; C23F 11/08**

[52] **U.S. Cl.** ..... **210/754; 210/764; 422/14; 423/511; 423/579; 8/107; 8/108.1; 8/109; 8/129; 8/115.68; 8/115.69; 8/137; 252/94; 252/186.21; 252/186.36; 252/186.37; 252/187.1**

[58] **Field of Search** ..... **210/764, 754, 210/749; 422/14; 423/511, 579; 8/107, 108.1, 109, 129, 115.68, 115.69, 137; 252/94, 186.21, 186.36, 186.37, 187.1**

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*Primary Examiner*—Neil McCarthy  
*Attorney, Agent, or Firm*—Kelly L. Cummings; Thomas M. Breiningner

[57] **ABSTRACT**

The invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

**21 Claims, No Drawings**

# PROCESS TO MANUFACTURE STABILIZED ALKALI OR ALKALINE EARTH METAL HYPOBROMITE AND USES THEREOF IN WATER TREATMENT TO CONTROL MICROBIAL FOULING

## FIELD OF THE INVENTION

The present invention relates to a method of preparing a stabilized alkali or alkaline earth metal hypobromite to control microbiological, more specifically, a stabilized sodium hypobromite solution the characteristics of which include non-volatility, high free halogen residual, lower bromate formation, reduced generation of absorbable organic halogen in process waters, as well as improved performance against biofouling.

## BACKGROUND OF THE INVENTION

Aqueous solutions of sodium hypochlorite are widely used in cooling water towers; bleaching processes; treatment of recreational waters including swimming pool water, water slide and other water game equipment, spas, and whirlpools; disinfectants; laundry detergents; and, industrial biocides including applications in the petroleum industry. However, a major disadvantage of NaOCl is its instability. As is well known in the art, several methods are used to stabilize NaOCl. The Self et al. reference (U.S. Pat. No. 3,328,294) described a continuous process to stabilize hypochlorite with an equal molar ratio of sulfamic acid. This process was improved upon by Rutkiewicz reference (U.S. Pat. No. 3,767,586) who added a buffer which aided in pH control increasing the stability of concentrated solutions.

Bromine has various advantages over chlorine for water treatment such as better performance in high pH or amine environments and a lower volatility. However, sodium hypobromite, the bromine analog to chlorine bleach, is not stable under typical storage conditions, and as such, is not commercially available. Instead, bromine is typically delivered to water treatment systems by various inefficient or inconvenient methods. The art described by either Self et al. or Rutkiewicz does not mention a method to stabilize the well known precarious sodium hypobromite molecule as disclosed within this invention. Also, this disclosure shall improve upon the art of Rutkiewicz by formulating a more stable, concentrated NaOBr solution in the absence of a buffer.

In one such bromine delivery method, NaBr is oxidized in situ by introducing gaseous chlorine or NaOCl into the process water stream. Another technique uses a stable perbromide ( $\text{Br}_3^-$ ) solution containing 30-40 percent bromine. The perbromide solution releases bromide and bromine when injected into water systems. The formed bromine hydrolyzes instantly to hypobromous and hydrobromic acids. Alternatively, bromine chloride may be added to aqueous process streams wherein it hydrolyzes to hypobromous and hydrochloric acids.

All of these bromine delivery systems have inherent disadvantages. Gaseous chlorine, perbromide, and bromine chloride have high halogen vapor pressures which present safety concerns in handling and storage. Also, these concentrated halogen solutions are corrosive to many metal surfaces found in process equipment either by their high vapor pressures or by the release of one mole of hydrohalic acids in water systems yielding localized low pH environments. As such, none of these methods provide a stable bromine product that can be safely and easily handled while meeting environmental requirements (more fully discussed

below), such as low bromate and absorbable organic halogen generation, and having a high free halogen residual and a low volatility (resulting in a greatly reduced odor and vapor-phase corrosion). In addition, a portion of the expensive bromine compound is wasted through an ineffective by-product in some delivery schemes. Thus, the need for a safe, convenient, economical, stable bromine water treatment product remains and is significant.

The Goodenough et al. reference (U.S. Pat. No. 3,558,503), teaches stabilization of bromine using any compound which reacted reversibly with bromine. The disclosed compounds include:

(a) water-soluble primary and secondary amines or amides; and,

(b) sulfamic acid and its water-soluble salts. However, the bromine solutions prepared according to the Goodenough et al. reference teachings are not stable enough for practical use in commercial cooling water, oil field and other industrial applications.

Sulfamic acid, according to the Goodenough et al. reference, is employed as a free acid or as one of its water-soluble salts such as the sodium, potassium or ammonium salt. However, the manner in which the bromine solutions are prepared provide relatively low stabilities and low available halogen concentrations compared with the discoveries claimed within this invention disclosure. The Goodenough et al. reference charges elemental bromine into aqueous solution prior to stabilization. Because elemental bromine is used in the process disclosed in the Goodenough et al. reference, this process is difficult to complete as well as potentially hazardous since elemental bromine is a fuming, corrosive, toxic liquid.

The Goodenough et al. reference mentions that the available bromine concentration immediately following preparation was about 1 percent by weight. The low bromine concentration achieved by this method was due in part to bromine being soluble at just 4 percent in cold water. Additionally, bromine is wasted in the process disclosed in the Goodenough et al. reference. The reaction according to this process is as follows:



Because the produced HBr does not function as a biocide, one half of the bromine adds nothing to the strength of the biocidal species, HOBr. This invention disclosure improves on the Goodenough et al. reference by means of a safer, easier, and more economical process.

Much higher levels of available halogen for disinfection were attained using the invention disclosed in this application, as shown in Table I below, by stabilizing the sodium salt (NaOBr) generated during manufacture. As previously mentioned, sodium hypobromite is unstable and therefore not commercially available. If a stabilized form of NaOBr is proposed, the stabilization process must occur quickly after NaOBr is made.

The method described in the Goodenough et al. reference could not achieve these increased bromine levels as the order of reagent addition described in the reference was deemed not critical to the operability of the method. Since NaOBr is synthesized by the following reaction,  $\text{NaOCl} + \text{NaBr} \rightarrow \text{NaOBr} + \text{NaCl}$ , addition of the stabilizer prior to bromide oxidation would not permit the formation of NaOBr.

When water is treated with many halogenated biocides, undesirable halogenated organics can be generated as by-products. These compounds are causing increased envi-

ronmental and health concerns. It is generally known that low molecular weight halogenated organics are more easily biologically degraded than higher molecular weight species. However, the low molecular weight forms may be more toxic to aquatic and mammalian organisms. Differentiation of these halogenated organics is costly, time consuming and requires the use of gas chromatography, high performance liquid chromatography or gel permeation chromatography. Absorbable Organic Halogen, "AOX", was chosen as a method of measuring the sum of halogenated organic compounds without speciation. AOX is used as an effluent monitoring parameter of water or wastewater in Europe and North America. In the United States, the Environmental Protection Agency ("EPA") is looking closely at AOX discharge in the pulp and paper industry. An object of the present invention is to provide a stable NaOBr solution that can be used to control microbial fouling with minimal AOX generation. The problems associated with controlling AOX levels, being a more recent developing environmental concern, have not been previously resolved in the industry.

The United States EPA extrapolates some animal carcinogenesis with the presence of low bromate levels found in drinking water. Bromate may appear from the ozonation of bromide-containing water raising some concerns in the drinking water industry. Bromate may also be formed by the disproportionation of hypobromite. This reaction occurs at a greater rate in alkaline environments. Hence, if bleach is added to a NaBr solution, the high pH environment could lead to the undesirable production of bromate. One use of the present invention, which was previously unknown and is surprising, is to greatly minimize bromate formation by stabilizing hypobromite when conditions are favorable for bromate production.

The petroleum industry experiences biological problems, including microbiologically influenced corrosion, both localized and general, in oil field waters. In addition, bacteria can plug the wellbore surface in waterflood injection wells. The bacteria form slime plugs, reducing injectivity. Treatment with stable bromine water is a convenient method of dealing with these and similar problems.

It is an object of the present invention to provide a process whereby aqueous solutions of sodium hypobromite can be produced which are relatively resistant to degradation and/or decomposition and which are relatively non-corrosive and non-volatile, yet which retain an improved capacity for oxidation and bactericidal activity.

Another object of the present invention is to provide a stable sodium hypobromite solution in which the formation of AOX is minimized while providing improved microbial fouling control. Other objects and advantages of the present invention will become obvious from the following description thereof.

#### SUMMARY OF THE INVENTION

The invention, according to one embodiment is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali

metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,

- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

One embodiment of the invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The amount of hypochlorite used will vary depending upon which hypochlorite salt is used.

The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 70 percent by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

Another embodiment of the invention is a stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and.

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The amount of hypochlorite used will vary depending upon which hypochlorite salt is used.

The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 70 percent by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

The invention can be used in an industrial water system. Such water systems would contain from about 0.05 to about 1000 ppm, more preferably from about 0.05 to about 10 ppm, and most preferably from about 0.1 to about 5 ppm of the stabilized aqueous solution of an alkali or alkaline earth metal hypobromite.

The invention can be used in the laundering of soiled garments where the soiled garments are washed in an aqueous media, such as water, containing a detergent and a bleaching agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the bleaching agent.

The invention can also be used in the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

The invention can be used in the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

The invention can be used in the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters. An anti-microbiofouling effective amount of stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be added to the produced oil field waters.

The invention can also be used in the control of microbiofouling in aqueous systems. An effective anti-

microbiofouling amount of stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be added to aqueous systems.

In another embodiment, the invention is a method of preventing microbiofouling on the surfaces of equipment in contact with in an industrial water system. The method comprises adding to the aqueous system an anti-microbiologically effective amount of a stabilized sodium hypobromite solution. The stabilized sodium hypobromite solution is prepared by the steps of:

a. Mixing an aqueous solution of sodium hypochlorite having from about 5 percent to about 30 percent available halogen (as chlorine) with sodium bromide;

b. Allowing the sodium bromide and the sodium hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized sodium hypobromite;

c. Adding to the unstabilized solution of sodium hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to sodium hypobromite of from about 0.5 to about 7; and.

d. Recovering a stabilized aqueous sodium hypobromite solution.

The industrial water systems include cooling water systems, cooling ponds, reservoirs, sweetwater applications, decorative fountains, pasteurizers, evaporative condensers, hydrostatic sterilizers and retorts, gas scrubber systems, and air washer systems.

Another embodiment of the invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution when the level of available halogen as chlorine is below about 5 percent. The method comprises the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and.

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

When the level of available halogen as chlorine is below about 5 percent, the amount of water in which the stabilizer, the alkali metal sulfamate, is dissolved into must be decreased. At this point, the amount of water is low enough that the alkali metal sulfamate is only sparingly soluble in the water. Therefore, the temperature of the aqueous alkali metal sulfamate solution must be maintained above 50° C. to keep the alkali metal sulfamate in solution until the solution is added to the aqueous solution of unstabilized sodium hypobromite. Once mixed with the sodium hypobromite solution, solubility is no longer a concern, and the resulting stabilized sodium hypobromite solution does not need to be maintained above 50° C.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The amount of

hypochlorite used will vary depending upon which of the hypochlorite is used.

The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 70 percent by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

Another embodiment of the invention is a stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and, d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

As discussed above, when the level of available halogen as chlorine is below about 5 percent, the amount of water in which the stabilizer, the alkali metal sulfamate, is dissolved into must be decreased. At this point, the amount of water is low that the alkali metal sulfamate is only sparingly soluble in the water. Therefore, the temperature of the aqueous alkali metal sulfamate solution must be maintained above 50° C. to keep the alkali metal sulfamate in solution until the solution is added to the aqueous solution of unstabilized sodium hypobromite. Once mixed with the sodium hypobromite solution, solubility is no longer a concern, and the resulting stabilized sodium hypobromite solution does not need to be maintained above 50° C.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The amount of hypochlorite used will vary depending upon which of the hypochlorite is used.

The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth

metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 70 percent by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

In another embodiment, the invention is a method of preventing microbiological fouling on the surfaces of equipment in contact with in an industrial water system. The method comprises adding to the aqueous system an antimicrobially effective amount of a stabilized sodium hypobromite solution. The stabilized sodium hypobromite solution is prepared by the steps of:

a. Mixing an aqueous solution of sodium hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with sodium bromide;

b. Allowing the sodium bromide and the sodium hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized sodium hypobromite;

c. Adding to the unstabilized solution of sodium hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to sodium hypobromite of from about 0.5 to about 7; and,

d. Recovering a stabilized aqueous sodium hypobromite solution.

As discussed above, when the level of available halogen as chlorine is below about 5 percent, the amount of water in which the stabilizer, the alkali metal sulfamate, is dissolved into must be decreased. At this point, the amount of water is low that the alkali metal sulfamate is only sparingly soluble in the water. Therefore, the temperature of the aqueous alkali metal sulfamate solution must be maintained at at least 50° C. to keep the alkali metal sulfamate in solution until the solution is added to the aqueous solution of unstabilized sodium hypobromite. Once mixed with the sodium hypobromite solution, solubility is no longer a concern, and the resulting stabilized sodium hypobromite solution does not need to be maintained at at least 50° C.

This invention provides several differences over the known art, including a specific order of addition in the manufacturing process whereby a stabilized sodium hypobromite solution is produced having improved stability, non-volatility, reduced bromate and AOX formation, improved microbiological control, and an increased free halogen residual in cooling water.

The stability of the stabilized hypobromite solution, as compared to the stabilized bromine disclosed in the Goodenough et al. reference and unstabilized sodium hypobromite in Table I, is greatly increased. Based on the surprising increased stability of the stabilized sodium hypobromite of this invention, it is apparent that the order of addition in the process of manufacture is critical.

**INCREASED STABILITY OVER PRIOR ART**  
**% LOSS OF AVAILABLE HALOGEN**

	After 4 days	After 14 days	After 21 days	After 34 days	After 84 days
Goodenough et al.	21	23	—	—	—
Stabilized Sodium Hypobromite	0	0	0	1	1
Unstabilized Sodium Hypobromite	—	74	79	84	93

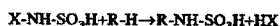
$$\underset{(X_{\text{free}})}{\text{HO-X}} + \text{H-NH-SO}_3\text{H} \rightleftharpoons \underset{(X_{\text{stable}})}{\text{X-NH-SO}_3\text{H}} + \text{H}_2\text{O}$$

The degree of stabilization is expressed as the concentration ratio of  $X_{stable}$  to  $X_{free}$ . The  $X_{free}$  concentration of the stabilized bromine was detectable while the concentration of the  $X_{free}$  for stabilized chlorine was not. It was concluded that the chlorine in the stabilized chlorine was completely stabilized while the bromine in the stabilized bromine exists in both free and stabilized forms. This contributes in part to the increased antimicrobial properties of stabilized NaOBr over stabilized NaOCl which will be described in more detail in Example 3.

### Pathway A: AOX formation by HOX



### Pathway B:



When stabilized chlorine is used as a biocide, only Pathway B is possible because no free HOCl exists in the system. Thus, no or very low AOX will be formed using this product (see Table II below).

Apparently, the proposed mechanism explains the cause of AOX reduction due to the use of stabilized halogen biocides. The mechanism should be applicable to other stabilized halogen products when ammonia, amines or amides are used as the stabilizing agents.

In order to reduce the AOX formation by a stabilized halogen biocide, it is preferable to select strong stabilizing agents so that Pathway B can dominate. However, the drawback to a very stable halogenated compound is the

The following examples are presented to describe preferred embodiments and utilities of the invention and are not 10 meant to limit the invention unless otherwise stated in the claims appended hereto.

### Example 1

### Preparation of Stabilized Sodium Hypobromite with a Critical Order of Addition

In order to demonstrate the constancy of stabilized NaOBr, solutions of sodium hypochlorite and sodium bromide were mixed forming NaOBr then stabilized with sodium sulfamate as described below. Sodium hypochlorite solution was diluted in demand-free water. This diluted solution was titrated by the DPD-FAS method. The available chlorine level present in the original solution was determined to be 15 percent. 42.4 grams of the neat NaOCl solution were added to 20.5 grams of a 45 percent NaBr solution. This reaction forms unstabilized NaOBr. The stabilization solution was formulated with 9.6 grams of sulfamic acid, 14 grams of water, and 13.2 grams of 50 percent sodium hydroxide. The stabilization solution is then added with stirring to the NaOBr. The order of addition is critical in this process which differs from the Goodenough et al. reference. For instance, if the stabilizer was added to NaOCl prior to NaBr introduction, the bromide would not be oxidized to hypobromite. Also, bromine solutions prepared in the manner referenced above gave more stable oxidizing species than the prior art. Bromine solutions stabilized as explained in the Goodenough et al. reference exhibited a decrease in halogen activity from an initial concentration of 1 percent to 0.77 percent after fourteen days representing an active ingredient loss of 23 percent. The stabilization procedure described here improved on the prior art as the decline of active ingredient was only 1 percent after 84 days (see Table I above). An unstabilized NaOBr solution prepared in an similar process by replacing sulfamic acid with distilled water lost 94 percent available halogen during the same period.

### Example 2

### Less AOX is Formed in Stabilized Halogen Solutions

AOX is a generic class of compounds which includes all organic molecules containing halogen. Limits for AOX discharge from cooling water systems have already been established in some European countries. To simulate AOX formation during stabilized and unstabilized sodium hypobromite action in cooling water, a mixed bacterial culture typically found in cooling water was cultivated in L-broth overnight and the cells harvested by centrifugation. The cell pellet was washed with synthetic cooling water (90 ppm calcium, 50 ppm magnesium, 110 ppm "M" alkalinity, pH 8.0-8.2) twice to remove the remaining organic medium. Cells were then resuspended into an equal volume of cooling water. A capped dark bottle served as the reactor. Synthetic cooling water was added to the bottle followed by the washed bacterial stock yielding approximately 10<sup>7</sup> cells/ml. Stabilized NaOBr or unstabilized NaOBr was dosed into this bacterial suspension at a final concentration of 1, 2, 3, or 4 ppm total halogen (as chlorine). Headspace in the bottle was minimized to avoid the evaporative loss of halogenated organics and the solution stirred for 24 hours to simulate a



typical cooling system. Immediately before AOX analysis, the sample was acidified to pH 2.0 with concentrated nitric acid. A Mitsubishi TOX-10 Analyzer was used according to US EPA Method 9020 to measure the AOX concentration in the samples. Ultrapure water was used for the preparation of all reagents and standard solutions to prevent any contamination. The amounts of AOX formed in each such treatment is shown in Table II below. Cooling water with stabilized NaOBr formed less AOX than treatments using unstabilized NaOBr at equivalent halogen concentrations. Linear regressions were performed on both sets of data to obtain linear-fit equations shown below for both stabilized and unstabilized NaOBr:

Stabilized NaOBr: AOX (ppb)=23.3 X Dose (ppm)

Unstabilized NaOBr: AOX (ppb)=53.9 X Dose (ppm)

Testing also showed that stabilization of NaOCl reduced AOX generation in cooling water dosed with two ppm total residual (see Table II).

TABLE II

AOX FORMATION (ppb) IN STABILIZED HALOGEN SOLUTIONS				
DOSE (ppm total halogen as chlorine)	ppb AOX Formed from Specified Halogen Source			
	Stabilized NaOBr	Unstabilized NaOBr	Stabilized NaOCl	Unstabilized NaOCl
1	29	56		
2	52	124	13	118
3	68	174		
4	91	197		

## Example 3

## Antibacterial Activity of Stabilized Sodium Hypobromite

Freshly prepared solutions of stabilized and unstabilized sodium hypobromite were diluted then added to cooling water in order to achieve a one ppm free halogen residual (as chlorine). Sodium hypochlorite was stabilized in the same fashion as described for NaOBr in Example One with the exception that NaBr was directly replaced with distilled water. Stabilized and unstabilized sodium hypochlorite were diluted then added to cooling water at a final concentration of one ppm free halogen residual (as chlorine). The volumes of all solutions needed to achieve a one ppm free halogen residual (as chlorine) was recorded. Following 6 and 21 days of dark storage, identical dilutions of stabilized and unstabilized sodium hypochlorite solutions were prepared and the volume originally required for a one ppm free halogen residual (as chlorine) was added to cooling water containing approximately  $10^6$  *Pseudomonas aeruginosa* cells/mL. Aliquots were extracted at 10 and 30 minutes into cooling water dilution blanks containing a halogen neutralizer (0.05 percent  $\text{Na}_2\text{S}_2\text{O}_3$ ) then enumerated on tryptone glucose extract agar. Stabilized NaOBr retained its antibacterial activity after storage while the unstabilized form lost its efficacy against *Pseudomonas aeruginosa* (see Table III below). The results were even more dramatic as the storage period increased. This effect was likely due to the disproportionation of the unstable hypobromite ion into the non-biocidal species bromide and bromate. Surprisingly, NaOCl stabilized in the same manner as NaOBr was comparatively ineffective under the conditions tested (Table III).

TABLE III

ANTIBACTERIAL ACTIVITIES OF STABILIZED & UNSTABILIZED HYPOHALITE SOLUTIONS AFTER 6 & 21 DAYS  
equivalent volumes initially required to achieve  
one ppm free halogen added throughout test

	% BACTERIA KILLED			
	6 DAYS OF STORAGE CONTACT TIME (MINUTES)		21 DAYS OF STORAGE CONTACT TIME (MINUTES)	
	10	30	10	30
stabilized NaOBr	99.9	100	99.8	100
unstabilized NaOBr	99.8	99.7	0.4	6.1
stabilized NaOCl	0	0	0	21.0
unstabilized NaOCl	100	100	100	100

## Example 4

## Depression of Bromate Formation Following Stabilization of Sodium Hypobromite

Hypochlorite ions are known to disproportionate into halate and halide under alkaline conditions. Halate ions are undesirable degradants being suspect carcinogens and are under consideration for governmental regulation. The reaction of NaBr with NaOCl can yield significant amounts of bromate in elevated pH environments. Surprisingly, the stabilization of NaOBr with sodium sulfamate greatly minimized bromate formation (see Table IV below). Stabilized and unstabilized sodium hypobromite solutions were prepared as described in Example One. These solutions were stored in the dark at room temperature during the course of the study. Eight month old samples of stabilized and unstabilized NaOBr, both maintained at pH 14, a condition suitable for bromate formation, were assayed for bromate. A Dionex 4000 series gradient ion chromatography system equipped with AG9-SC/AS9-SC columns and a conductivity detector was used to measure the bromate concentration in the samples. The chromatograph was operated according to a method currently under investigation by the EPA for the analysis of bromate in ozonated drinking water. Purified water from an Interlake Water Systems deionization system was used for the preparation of all reagents and standard solutions to prevent contamination.

TABLE IV

BROMATE FORMATION IN STABILIZED & UNSTABILIZED NaOBr SOLUTIONS STORED FOR EIGHT MONTHS

	STABILIZED NaOBr	UNSTABILIZED NaOBr
PERCENT BROMATE	0.004	2.700

As noted above, the pH of these solutions was high which favors bromate formation. However, NaOCl, which contains significant amounts of NaOH, is typically diluted with system water prior to the introduction of the bromide species in most industrial applications. The pH of this diluted system would be lower than the neat NaOCl/NaBr formulation described above theoretically minimizing bromate formation. The available chlorine in a NaOCl sample diluted (1:100) with distilled water was titrated by the DPD-FAS method. A solution of 45 percent sodium bromide was added

to the dilute NaOCl at a molar ratio of 1 Cl<sub>2</sub>:1 Br<sup>-</sup> forming NaOBr. This reaction proceeded for thirty minutes. Then, appropriate volumes of this dilute NaOBr solution were added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as Cl<sub>2</sub>) as determined by the DPD-FAS method. Similarly, a dilution of stabilized sodium hypobromite (1:100) was made in distilled water. Dilute stabilized NaOBr was added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as Cl<sub>2</sub>) as determined by the DPD-FAS method. Bromate analysis then proceeded in the manner described above. Bromate was not detected in any of the cooling water samples dosed with either stabilized or unstabilized dilute NaOBr at typical use concentrations. These results signify the safety factor for bromate built into the stabilized sodium hypobromite formulation as well as the industrial in situ oxidation of NaBr with dilute NaOCl.

#### Example 5

Use of Stabilized NaOBr Increased the Percentage of Free Residual in a Recirculating Cooling Water System Compared to Other Stabilized Halogen Compounds

A major drawback to some commercial stabilized chlorine products for industrial water treatment is the low percentage of free chlorine residual delivered to the water system. This effect is due to the strength of the chemical bond between the stabilizer, usually a nitrogenous compound, and chlorine. Chloramines, i.e. combined chlorine, are weaker microbicides than free chlorine. However, bromamines are considered to be nearly as effective against microorganisms as free bromine. Thus, it is essential to have a high percentage of the total available halogen in the free form when chlorine products are employed. Conversely, this phenomenon is not as crucial when employing stabilized NaOBr. A commercial heating, ventilation and air conditioning ("HVAC") cooling system was sequentially treated with stabilized NaOCl, a bromochloroalkylhydantoin, and finally stabilized NaOBr. There was a low percentage of free chlorine relative to total available halogen present in the stabilized NaOCl treated system (see Table V below). A lower percentage of free halogen was measured when a different stabilization system, an alkylhydantoin, was employed with bromine and chlorine (see Table V below). However, when stabilized NaOBr was fed into this system, the percentage of free available halogen relative to the total residual measured quickly increased (see Table V below). These phenomena imply that less stabilized NaOBr is required to obtain a free available halogen residual than the equivalent amount of stabilized NaOCl.

TABLE V

FREE RESIDUAL OXIDANT AS A PERCENT OF TOTAL RESIDUAL OXIDANT IN RECIRCULATING COOLING WATER SYSTEM

Days in System	Average Free Oxidant as a Percent of Total Residual Oxidant	Biocide Employed
36	13	stabilized NaOCl
45	9	halogenated hydantoins
33	53	stabilized NaOBr

#### Example Six:

Stabilization of Sodium Hypobromite Reduces Volatility

If a biocide is highly volatile, its performance may be adversely affected. For example, the biocide may flash off in the highly aerated conditions of a cooling tower or an air washer. This would lower the biocide concentration in the cooling water wasting the product. Halogen volatility also

leads to vapor-phase corrosion of susceptible equipment surfaces. In addition, halogen volatility may cause worker discomfort due to the "swimming pool" aroma. Thus, the need for an efficacious oxidizing biocide with low volatility is evident.

Concentrated solutions of either NaOCl, NaOBr, or stabilized NaOBr were added to a beaker. Halogen vapors were detected from the NaOCl and NaOBr solutions. No odors were noticed from the stabilized NaOBr. This is an improvement over existing products by minimizing halogen odors in product storage areas.

Bleach, NaOCl, is not commonly used in air washer systems due to some of the reasons listed above. Once an effective microbial control dose is achieved, the halogen odor may be so overwhelming that workers would not be able to comfortably operate in the treated areas. The low volatilization of stabilized NaOBr overcomes this drawback. Stabilized sodium hypobromite was added at elevated use concentrations to two textile mill air washers in order to investigate its volatility. Then the air was monitored throughout the mill. A Sensidyne air monitoring device outfitted with halogen detection tubes was used to instantaneously detect halogen in the air. The lower detection limit was 50 ppb which is below the Threshold Limit Value-Short Term Exposure Limit for bromine as established by OSHA. In addition, halogen badges were placed throughout textile mills in order to detect halogen vapors over extended periods of time. Neither monitoring system detected any halogen present in the air following the elevated stabilized NaOBr dose. No halogen odors were encountered in either the air washer unit or the return air. The microbial population was enumerated before and after stabilized NaOBr addition. The microbial population following dosing was reduced by greater than one order of magnitude. This example demonstrates the utility of stabilized sodium hypobromite in controlling the bacterial population while adding no halogen odor to the system area.

Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

We claim:

1. A method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution comprising:

- Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,
- Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

2. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, and calcium hypochlorite.

3. The method according to claim 1, wherein the bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid.

15

4. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

5. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite.

6. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

7. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 1 to about 30 percent by weight sodium hypobromite.

8. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 4 to about 15 percent by weight sodium hypobromite.

9. The method according to claim 7, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 8 to about 14.

10. The method according to claim 8, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 11 to about 14.

11. The method according to claim 9, wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 4.

12. The method according to claim 10 wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 2.

13. A stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

14. An industrial water system containing from about 0.05 to about 1000 ppm of the solution of claim 13.

16

15. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprises using as the bleaching agent the solution of claim 13.

16. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprises using as the oxidizing agent the solution of claim 13.

17. In a method for the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling, the improvement comprises using as the oxidizing agent the solution of claim 13.

18. In a method for the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprises adding to the produced oil field waters an anti-microbiofouling effective amount of the solution of claim 13.

19. A method of controlling microbiofouling in an aqueous system which comprises adding to the aqueous system an effective, anti-microbiofouling amount of the solution of claim 13.

20. A method of preventing microbiofouling on the surfaces of equipment in contact with in an industrial water system which comprises adding to the aqueous system an anti-microbiologically effective amount of a stabilized sodium hypobromite solution, said solution having been prepared by the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of sulfamate to hypobromite of from about 0.5 to about 7; and,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

21. The method according to claim 20, wherein the industrial water system is selected from a group consisting of: a cooling water system; a sweetwater system; a gas scrubber system; and, an air washer system.

\* \* \* \* \*

# APPENDIX

## H

# United States Patent [19]

Smyk et al.

[11] Patent Number: 4,992,209

[45] Date of Patent: Feb. 12, 1991

[54] METHOD FOR INHIBITING CORROSION  
IN COOLING SYSTEMS AND  
COMPOSITIONS THEREFOR,  
CONTAINING A NITRITE CORROSION  
INHIBITOR AND BROMOSULFAMATE

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[21] Appl. No.: 427,535

[22] Filed: Oct. 26, 1989

[51] Int. Cl.<sup>5</sup> ..... C23F 11/08

[52] U.S. Cl. .... 252/387; 252/389.62

[58] Field of Search ..... 252/388, 392, 391, 387,  
252/389.62; 423/388

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## [57] ABSTRACT

The method of adding to a nitrite corrosion inhibitor composition an effective amount of a bromosulfamate which is stable with respect to the nitrite corrosion inhibitor and provides an effective biocide, bactericide and fungicide. The composition using this bromosulfamate component to nitrite is utilized at about 0.1 to 10 ppm (residual) with an optimum of about 0.2 ppm of bromosulfamate. The bromosulfamate composition comprises reacting together sodium bromide (NaBr), sodium hypochlorite (NaOCl) or chlorine, and sodium sulfamate (NaSO<sub>3</sub>NH<sub>2</sub>) or sulfamic acid, and using the product "fresh" in treating the nitrite solution.

5 Claims, No Drawings

# METHOD FOR INHIBITING CORROSION IN COOLING SYSTEMS AND COMPOSITIONS THEREFOR, CONTAINING A NITRITE CORROSION INHIBITOR AND BROMOSULFAMATE

The term nitrite corrosion inhibitor applies to a wide group of inhibitors useful in industry, in metals such as steel, in closed and open recirculating systems of many types. These inhibitors, which contain nitrite, usually contain as an active ingredient a water-soluble nitrite salt, such as sodium nitrite. These nitrites may be converted to molecular nitrogen or ammonia by denitrifying bacteria and fungi. The present invention is designed to solve a problem presented in the art of how to keep the effective strength of the nitrite containing corrosion inhibitor composition in the presence of deleterious bactericides and fungicides.

The bromosulfamate compound specifically is one of a class of compounds constituting antimicrobial agents with particular reference as a bactericide and fungicide. Chlorine, bromine, and iodine compounds have been utilized, but the novelty is narrowing utilization to uncover a compound which is inert to or does not oxidize the nitrite corrosion inhibitor composition. The preferred bromosulfamate utilized as a liquid is preferably used in a range of about 0.1 to 10 ppm (residual) with an optimum of about 0.2 ppm.

The feed amount of the bromosulfamate which is the input of the treatment compound to the nitrite composition is 5 ppm. The residual is that product which is left of the bromosulfamate after mixing with the nitrite composition.

The bromosulfamate treatment composition is prepared from sodium bromide, sodium hypochlorite (or chlorine), and sodium sulfamate (or sulfamic acid) mixed together at ambient temperature or higher. The product bromosulfamate is prepared and utilized "fresh," where "fresh" is defined as up to five hours, as a biocide in the nitrite solution and therefore must be used soon after preparation.

## BACKGROUND OF THE INVENTION

The prior art points out a few distantly related patents as follows:

"Method for Prevention of Phosphonate Decomposition by Chlorine," U.S. Pat. Nos. 4,642,194 and 4,711,724; also "Use of Sulfamic Acid to Inhibit Phosphonate Decomposition by Chlorine-Bromine Mixtures," U.S. Pat. No. 4,759,852.

The sulfamate form noted in the '852 patent halts decomposition of phosphonates, whereas the bromide does not, and the application is to the decomposition of the phosphonates which is not in the present invention. However, the art shown above in the patents noted does not teach the idea of adding bromosulfamate, which does not oxidize nitrite and has excellent biocidal properties.

## Example I

This method has been tested on small scale where bromine residuals could be maintained without destroying nitrite. A test showed that without sulfamic acid, nitrite was destroyed when bromine was added to the system. Previous tests showed that chlorine destroyed nitrite and that chlorosulfamate did not destroy nitrite. However, chlorosulfamate is not as strong a microbio-

cidal agent as bromosulfamate, and the bromosulfamate compound is preferred.

Two pilot cooling tower tests have further confirmed these results. Test results:

System	Oxidant Residual (ppm)	% NO <sub>2</sub> -Oxidized
Chlorine	0.20	>90%
Bromine	0.20	>90%
Chlorosulfamate	0.05	<10%
Bromosulfamate	0.20	<10%

In these tests, when chlorine was used as the biocide, fed at approximately 50 ppm, 0.2 ppm of chlorine residual was maintained, but >90% of the nitrite was oxidized.

A similar result occurred when bromine was used, fed at approximately 50 ppm, 0.2 ppm of bromine residual was maintained, but >90% of the nitrite was also oxidized.

When chlorosulfamate was used, fed at approximately 5 ppm, only a trace, or about 0.05 ppm, of chlorine residual was maintained, but less than 10% of the nitrite was oxidized.

Utilizing bromosulfamate, fed at approximately 5 ppm, maintained 0.2 ppm of bromosulfamate residual, and less than 10% of the nitrite was oxidized.

The concentration of feed for chlorosulfamate and bromosulfamate was much less than the concentration of feed for the chlorine and bromine.

It should be pointed out that bromosulfamate is at least equal to chlorine and bromine in oxidant residual recovery, but chlorine and bromine are not useful biocides in the system because they destroy nitrite. Chlorosulfamate does not destroy nitrite but is not as effective a biocide as bromosulfamate.

## Example II

### Preparation of the Bromosulfamate Treatment Composition

50-200 grams of sodium bromide, NaBr, was added to 75 grams of sodium hypochlorite, NaOCl. After mixing the solution for 15-60 seconds, 50-200 grams of sodium sulfamate, NaSO<sub>3</sub>NH<sub>2</sub>, was added to the solution. The resulting composition was usable as a biocide.

This procedure is all prepared in solution. Additionally, it has been found that "fresh" treatment composition is of great importance since the oxidizing biocide system is not stable to be transported or preserved.

We claim:

1. A method of inhibiting corrosion comprising adding to a cooling system containing a nitrite corrosion inhibitor of an effective amount of bromosulfamate as a bactericide and fungicide.

2. The method of claim 1 wherein the effective amount of bromosulfamate is about 0.1 to 10 ppm (residual) with an optimum of about 0.2 ppm.

3. A nitrite containing corrosion inhibitor composition containing an effective amount of a bromosulfamate as a bactericide and fungicide.

4. The composition according to claim 3 wherein the effective amount of bromosulfamate is about 0.1 to 10 ppm (residual) with an optimum of about 0.2 ppm.

5. A method of making a nitrite containing corrosion inhibitor comprising adding the reaction product of sodium bromide, sodium hypochlorite or chlorine and sulfamate as a fresh solution wherein fresh is defined as being produced in one to 5 hours.

\* \* \* \* \*

# APPENDIX

## I



US007045153B2

**(12) United States Patent**  
**Howarth et al.****(10) Patent No.: US 7,045,153 B2**  
**(45) Date of Patent: May 16, 2006****(54) HIGHLY CONCENTRATED BROMINE COMPOSITIONS AND METHODS OF PREPARATION****(75) Inventors:** Jonathan N. Howarth, Modesto, CA (US); Michael S. Harvey, Modesto, CA (US)**(73) Assignee:** Enviro Tech Chemical Services, Inc., Modesto, CA (US)**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 194 days.**(21) Appl. No.:** 10/609,280**(22) Filed:** Jun. 27, 2003**(65) Prior Publication Data**

US 2004/0262239 A1 Dec. 30, 2004

**(51) Int. Cl.**  
**A01N 59/00** (2006.01)**(52) U.S. Cl.** ..... 424/723**(58) Field of Classification Search** ..... 424/723;  
252/186.1, 186.43, 187.2

See application file for complete search history.

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*Primary Examiner*—Betsey Morrison Hoey*(74) Attorney, Agent, or Firm*—Audrey A. Millemann;  
Weintraub Genshlea Chediak**(57) ABSTRACT**

Liquid and solid bromine-containing compositions are described. A liquid mixed halogen composition is also described. The highly concentrated liquid compositions and the high-activity solid compositions have excellent physical and chemical stability. The compositions are effective biocides in water treatment. Methods of preparing the compositions are also disclosed. These include combining a bromine compound in the oxidation state of -1 with hydrogen peroxide and a complexing agent followed by the addition of an alkaline source. The methods may further include the use of a solid organic or solid inorganic halogenating agent, conducting a solid-liquid separation, and adding an alkaline source.

**71 Claims, No Drawings**



# 1

## HIGHLY CONCENTRATED BROMINE COMPOSITIONS AND METHODS OF PREPARATION

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The invention relates to liquid and solid bromine-containing compositions, and a liquid mixed halogen bromine and chlorine-containing composition, for use as biocides in water treatment. The highly concentrated liquid compositions and high-activity solid compositions have excellent physical and chemical stability. The invention also relates to methods of preparing the liquid and solid compositions.

#### 2. Description of the Related Art

There are many ways of delivering a biocidal dose of bromine into water systems where the growth of microorganisms must be controlled. Early examples of accomplishing this involved introducing elemental liquid bromine ( $\text{Br}_2$ ) or liquid bromine chloride ( $\text{BrCl}$ ) to the water requiring treatment. However, both liquids are very volatile and evolve copious amounts of highly toxic and corrosive bromine fumes under normal conditions. Therefore, elaborate and expensive storage, transportation and handling safeguards must be practiced when using these products. It is hardly surprising that the high costs of managing these hazardous properties have rendered the use of elemental liquid bromine and liquid bromine chloride obsolete in most water disinfection applications.

An alternative system that overcomes these limitations employs an aqueous solution of sodium bromide ( $\text{NaBr}$ ) in conjunction with liquid sodium hypochlorite ( $\text{NaOCl}$ ) bleach. The user feeds the two materials to a common point where the  $\text{NaOCl}$  oxidizes the bromide ion to yield a mixture of hypobromous acid ( $\text{HOBr}$ ) and hypobromite ( $\text{OBr}^-$ ) ion. This activated solution must then be quickly introduced to the water being treated because the species in solution are unstable to the following rapid disproportionation and decomposition reactions.



Such reactions are undesirable because the products of the reactions ( $\text{HBr}$ ,  $\text{O}_2$  and  $\text{BrO}_3^-$ ) are not biocidally active.

Many users of this technology indicate that metering of two separate solutions of  $\text{NaBr}$  and  $\text{NaOCl}$  is especially inconvenient since two sets of pumps, flowmeters, valves, pipe work, and container dikes are necessary. In addition, the activation system must be designed so that sufficient time is allowed for the  $\text{NaBr}$  and  $\text{NaOCl}$  solutions to fully react prior to being injected into the water being treated. Another disadvantage is that  $\text{NaOCl}$  solutions deteriorate rapidly, and so delivery pumps must continually be readjusted to compensate and ensure that the correct proportions of reactants are maintained for accurate dosing. This dual  $\text{NaBr}/\text{NaOCl}$  activation system is so cumbersome and difficult to control that many users have demanded a system in which the  $\text{NaBr}$  is supplied in a pre-activated, one-drum form that is stabilized to disproportionation and decomposition reactions. Clearly, a single feed liquid bromine biocide with these properties would be far more convenient and easier to use and control than the dual component approach.

# 2

One of the earlier attempts to develop a single feed, liquid bromine biocide is described in U.S. Pat. Nos. 4,886,915 and 4,966,716 to Favstritsky, et al. An aqueous solution containing 38% elemental bromine complexed as ethanalammonium hydrogen perbromide was administered to the water being treated. Subsequently, U.S. Pat. No. 5,141,652 taught the use of strong solutions of halide salts and hydrohalic acids to form solutions of bromine chloride complexes. However, neither technology became fully commercialized because the problem of bromine fuming from the products was not completely alleviated.

U.S. Pat. Nos. 5,683,654, 5,795,487, 5,942,126, and 6,136,205 describe processes to manufacture a single feed, liquid bromine biocide by mixing aqueous hypochlorite solutions with bromide ion sources and then stabilizing this reaction mixture to disproportionation and decomposition by introduction of a stabilizing agent. Although the resultant solutions did not evolve bromine fumes, the process required a complex two-step reaction. In the first step,  $\text{NaBr}$  and  $\text{NaOCl}$  solutions were mixed and sufficient time was allowed to permit the formation of a  $\text{NaOBr}$  solution. In the second step, this was then introduced to a solution of the stabilizing agent maintained at  $50^\circ\text{C}$ . However, the main limitation of this approach lay in the use of a  $\text{NaOCl}$  bleach solution as the foundation of the process. When  $\text{NaOCl}$  bleach was used as the activating agent, the concentration of the stabilized bromine product became limited by the concentration of  $\text{NaOCl}$  bleach that is commercially available. In fact, despite using the highest strength grades of industrial  $\text{NaOCl}$  bleach, the bromine content of the resulting stabilized solutions was only about 14% as  $\text{Br}_2$  (6.3% as  $\text{Cl}_2$ ).

Moore et al. overcame the complexity of the two-step reaction in U.S. Pat. Nos. 6,068,861, 6,495,169, and 6,322,822 and disclosed a single vessel reaction in which bromine or bromine chloride was added to a halogen stabilizer solution under conditions of pH control. The available bromine content of the resultant solutions was reported to be at least 10% as  $\text{Br}_2$  (4.4% as  $\text{Cl}_2$ ). However, when the process was scaled up, as disclosed in U.S. Pat. Nos. 6,299,909, 6,306,441, and 6,348,219, it was found necessary to employ a three-reactor sequence, and an upper limit of 18% as  $\text{Br}_2$  (8% as  $\text{Cl}_2$ ) was imposed as the highest strength concentrate that could be made by the process. Another drawback to the processes described by Moore et al. was the hazardous nature of the starting reagents involved. The high cost of transporting and handling of elemental bromine or bromine chloride meant that commercial manufacturing of the stabilized bromine solutions could only be accomplished in highly specialized, dedicated plants close to sites where bromine is recovered from naturally occurring brines. In the U.S., the process of Moore et al. could only be practiced economically in manufacturing plants close to the brine fields of southern Arkansas or Michigan.

Yang et al. sought to increase the concentration of the available bromine in the stabilized formulation, and disclosed processes in U.S. Pat. Nos. 6,156,229, 6,423,267, and 6,287,473 that also employed the use of elemental bromine, bromine chloride, or sodium bromate. Using these methods, liquid bromine concentrates containing 26.2% as  $\text{Br}_2$  (11.6% as  $\text{Cl}_2$ ) were prepared. However, it was reported that such solutions were physically unstable, and large amounts of bromine-containing solids precipitated out of solution on standing overnight. Upon filtration of the solids, the liquid phase comprised 18.7% as  $\text{Br}_2$  (8.3% as  $\text{Cl}_2$ ). No information on the long-term chemical stability of the concentrates was reported. Other efforts to prepare stabilized liquid bromine formulations of high concentration were disclosed

in U.S. Pat. No. 6,270,722 where high strength industrial grade sodium hypochlorite solutions and gaseous  $\text{Cl}_2$  were used to oxidize sodium bromide solutions. Stabilized liquid bromine concentrates containing up to 20.75% as  $\text{Br}_2$  (9.22% as  $\text{Cl}_2$ ) were reported, but no information regarding the stability of the products to precipitation of solids was disclosed.

As is well noted in the prior art, the bromine content of stabilized formulations prepared using only sodium hypochlorite bleach solutions is limited by the strength of commercially available material. Indeed, even using the highest strength grade of industrial  $\text{NaOCl}$  bleach, the bromine content of the resulting solutions is reported to be only around 14% as  $\text{Br}_2$  (6.3% as  $\text{Cl}_2$ ). Although higher concentration solutions can be prepared with processes that employ  $\text{Br}_2$ ,  $\text{BrCl}$ , or  $\text{Cl}_2$ , those processes result in a substantial amount of halide ion salt contaminants. Typically, when using these reagents, half of the respective Br atoms, and all of the respective chlorine atoms, materialize as halide ion salts. These halide ion salts are soluble and remain in the solution. These halide ion salts are deleterious because they: (1) limit the concentration of stabilized liquid bromine that can be attained in solution; (2) decrease the chemical stability of the resulting liquid bromine concentrates; and (3) decrease the physical stability of the liquid bromine concentrate resulting in undesirable precipitation of salts from solution.

Certainly, the physical and chemical stability of the liquid bromine solutions was of concern to McKinnie, et al. in U.S. Pat. No. 6,506,418. They reported that under the acidic conditions advocated in their earlier processes based on  $\text{BrCl}$ ,  $\text{Br}_2$ , or  $\text{Cl}_2$ , "a substantial portion of the sulfamate can be hydrolyzed rather rapidly to sulfate" (col. 3, line 67 to col. 4, line 1) and further that "loss of sulfamate due to hydrolysis to sulfate can result in decreased storage stability of the finished product" (col. 4, line 3 to col. 4, line 5), later to point out that "loss of sulfamate imposes an economic burden on the operation" (col. 4, line 8 to col. 4, line 9). To overcome these deficiencies, acidic reaction conditions were discouraged, and alkaline pH conditions of 8-10 were recommended when introducing  $\text{BrCl}$ ,  $\text{Br}_2$ , or  $\text{Cl}_2$  to the reaction medium. Yang et al. also recognized the benefits of alkaline conditions in U.S. Pat. Nos. 6,123,870 and 6,287,473 for processes to prepare liquid bromine solutions. In these processes,  $\text{BrCl}$  or  $\text{Br}_2$  was added to highly caustic solutions of sodium sulfamate such that the resulting solution had a pH of 12.5. It was claimed that without adequate pH control, rapid decomposition of the oxidizing species occurred.

Users of stabilized liquid bromine products recognize that formulations that contain higher levels of active ingredients have distinct economic advantages over dilute products since less product needs to be applied to a water system in order to achieve the equivalent dose of a weaker material. Also, more concentrated products need to be replaced less frequently than dilute products. Other advantages of concentrated liquids include reduced packaging, storage, and transportation costs per unit weight of active ingredient. Products prepared to contain high levels of dissolved active ingredients must display two essential attributes. First, they must be chemically stable, i.e. they should not decompose quickly, so as to maintain high activity for extended periods. Second, they must be physically stable, i.e. they should not precipitate or crystallize into solid salts that could plug pipe work and make the feeding of liquid materials grind to a halt.

Therefore, the need exists for liquid biocidal bromine compositions of higher concentration and superior physical

and chemical stability than those described in the prior art and for methods of preparation of such compositions. There is a need for methods that employ inexpensive starting materials that are less hazardous and easier to handle than elemental liquid  $\text{Br}_2$  or liquid  $\text{BrCl}$ . There is also a need for methods that are not restricted to manufacturing plants close to bromine recovery facilities and that may be conducted quickly and efficiently in a single reactor. This invention addresses these needs.

Additionally, there is a need for liquid biocidal compositions based on mixtures of bromine and chlorine. No such compositions have ever been reported. All of the prior efforts have been directed toward the preparation of compositions in which bromine is the sole active ingredient, primarily because of the superior biocidal performance of bromine compounds compared to chlorine compounds. In waters exerting a high halogen demand, however, it is more economical for the demand to be satisfied with lower cost chlorine chemistry than with higher cost bromine chemistry. Thus, there is a need for a liquid composition containing both bromine and chlorine. This invention addresses this need as well.

There is also a need for a solid high-activity bromine-containing biocidal composition that is stable and fast dissolving. There are several solid, high-activity bromine-releasing compounds that are sold commercially as biocidal products. They are generally available as heterocyclic organic compounds to which an oxidizing bromine atom is covalently bonded to a nitrogen atom on the ring. Examples include N,N' bromochloro-5,5-dimethylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, and mixtures of these compounds with various other components. In water, these materials hydrolyze to release hypobromous acid, which is the biocidal agent. However, the major limitation of these solid compounds is that they are only sparingly soluble in water. Indeed, N,N' bromochloro-5,5-dimethylhydantoin has a water solubility of only 0.1% at 20° C. As a result, bromine is only released very slowly from these products as they dissolve. This is a significant disadvantage when the water requires treatment with a high, rapid dose of biocidal bromine as is necessary in shock and slug dosing procedures. Therefore, there exists the need for solid, high-activity forms of bromine of high water solubility and which dissolve rapidly and completely to provide the water with a high, rapid dose of biocidal bromine. Additionally, these solid products must have a long shelf life and not lose activity prior to use. This invention addresses these needs.

#### SUMMARY OF THE INVENTION

The present invention is directed to methods of preparing highly concentrated liquid bromine-containing compositions and highly concentrated mixed halogen liquid bromine and chlorine-containing compositions, and high-activity solid bromine-containing compositions that have excellent physical and chemical stability. The invention is also directed to the compositions themselves.

The compositions of this invention are sources of oxidizing halogen that are useful for microbiological control in aqueous systems. This is generally achieved by introducing the compositions into water requiring microbiological control in an amount sufficient to be biocidally effective. Application areas include a number of industrial water systems such as recirculating cooling water, once-through cooling water, air washer systems, decorative fountains, oil field injection water, oil well completion fluids, municipal and industrial wastewater, brewery pasteurizing water, hydro-

5

static sterilizer cooling water, pulp and paper processing water, and agricultural irrigation water. Application areas also include a number of residential water systems where the home consumer can apply the compositions in aqueous systems where microbiological control is necessary. Some of these consist of pool and spa water, kitchen and bathroom rinses, toilet bowl rinses, and mold and fungus sprays for inside and outside the home.

The first, second, and third embodiments of the invention are methods for preparing liquid bromine-containing compositions. In the first embodiment, anhydrous hydrogen bromide gas and a concentrated solution of hydrogen peroxide are used to make a liquid composition. In the second embodiment, an aqueous solution of bromide ions, a concentrated solution of hydrogen peroxide, and a solid halogenating agent (either organic or inorganic) are used to make a liquid bromine-containing composition or a mixed halogen liquid bromine and chlorine-containing composition. In the third embodiment, an alkali metal or earth alkali metal solution of bromide ions is combined with a solid halogenating agent (either organic or inorganic) to make a liquid bromine-containing composition or a mixed halogen liquid bromine and chlorine-containing composition.

The fourth and fifth embodiments of the invention are methods for preparing solid bromine-containing compositions. The fourth embodiment utilizes a bromine compound in the oxidation state of -1, a concentrated solution of hydrogen peroxide, and a solid halogenating agent (either organic or inorganic). The fifth embodiment utilizes an alkali metal or earth alkali metal solution of bromide ions and an organic halogenating agent. Both the fourth and fifth embodiments may be used to prepare two end products. The first is a saturated solution of the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate. The second is the solid alkali metal or earth alkali metal salt of hydrated (or anhydrous) N-bromosulfamate.

The sixth, seventh, and eighth embodiments of the invention are compositions of matter. The sixth embodiment is a highly concentrated bromine-containing liquid composition having an active ingredient content of at least about 18% as  $\text{Br}_2$  (8% as  $\text{Cl}_2$ ). This liquid has zero to about 1 mole of dissolved halide ion salts per mole of active halogen, depending on the method of preparation. Further, this liquid composition has physical stability in that it is not prone to solid precipitates and is stable to at least three cycles of freezing and thawing and has chemical stability in that its active ingredient half-life is at least about 58 days at 125° F. The liquid also has undetectable levels of bromate ion.

The seventh embodiment is a composition of matter, a highly concentrated mixed halogen liquid composition containing both bromine and chlorine, having an active ingredient content of at least about 11.25% as  $\text{Br}_2$  (5% as  $\text{Cl}_2$ ). It is characterized as containing less than about 1 mole of dissolved halide ion salts per mole of active halogen. Compared to the all-bromine composition of the sixth embodiment, the mixed halogen composition has even greater physical and chemical stability.

The eighth embodiment is two compositions of matter: the solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate and the solid alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate. These high-activity solids are stable and dissolve quickly to yield a highly concentrated bromine-containing solution.

A significant advantage of this invention is that it provides stable, aqueous bromine-containing compositions that contain significantly lower amounts of contaminant halide ion salts than the methods of the prior art. The methods of the

6

first and second embodiments result in liquid compositions that possess little or no halide ion salts because all or significantly all oxidation is accomplished with high strength hydrogen peroxide solutions. Contrary to processes that employ  $\text{NaOCl}/\text{NaBr}$  solutions,  $\text{Cl}_2/\text{NaBr}$  solutions,  $\text{Br}_2$ , or  $\text{BrCl}$ , hydrogen peroxide solutions contribute no inert ions or extraneous salts to the finished product that adversely impact its strength and stability. Thus, the methods of these embodiments minimize halide ion-induced physical and chemical destabilization. Assuming a 100% reaction yield, Table I compares the ratio of inactive, soluble halide ( $\text{X}^-$ ) ion to active bromine that materializes with the product when various reagents are used.

TABLE I

Reagent	Moles dissolved $\text{X}^-$ ion/mole stabilized active bromine
$\text{Br}_2$	1
$\text{BrCl}$	1
$\text{NaOCl}/\text{NaBr}$	2
$\text{Cl}_2/\text{NaBr}$	2
Present invention	0-0.8

Another notable advantage of this invention is that it makes possible the formation of highly concentrated liquid and high-activity solid bromine-containing compositions using inexpensive reagents. For example, the method of the first embodiment (yielding a liquid composition) and the method of the fourth embodiment (yielding a solid composition) may use anhydrous hydrogen bromide gas. This gas is a by-product of chemical reactions in which organic compounds are brominated with elemental  $\text{Br}_2$ . Gaseous anhydrous hydrogen bromide escapes the reactor and is normally scrubbed into water to form a solution of 48%-70% aqueous hydrogen bromide solution that is either piped to a separate unit operation for production of more elemental  $\text{Br}_2$ , or is neutralized and disposed of as waste. The methods of the first, second, and fourth embodiments also use an inexpensive oxidizing agent, hydrogen peroxide.

A major benefit of the methods of the second, third, fourth, and fifth embodiments is that they use solid halogenating agents. Because solid halogenating agents are devoid of water, the bromine content of the finished compositions is not diluted as it is where hypochlorite solutions are used. Further, these solid halogenating agents are generally high in available halogen and do not contain large amounts of extraneous salts or inactive ingredients that enter the finished product. Hence, the compositions that are obtained using solid halogenating agents possess lower levels of water, as well as lower levels of dissolved salts or other extraneous materials, which would otherwise dilute the available bromine content of the product and adversely impact its chemical and physical stability.

Another remarkable benefit of this invention is that the methods of the second and third embodiments make possible the formation of highly concentrated liquid bromine-containing compositions employing processes that generate no solid wastes. Thus, using solid organic halogenating reagents such as trichloroisocyanuric acid (TCCA) (also known as trichloro-s-triazinetriene), sodium dichlorisocyanurate (NaDCC) (also known as sodium dichloro-s-triazinetriene), or sodium dichlorisocyanurate dihydrate ( $\text{NaDCC} \cdot 2\text{H}_2\text{O}$ ) (also known as sodium dichloro-s-triazinetriene dihydrate), the by-product of the halogenation reaction is cyanuric acid (CA). This is insoluble in the reaction medium and precipitates in a solid form. Upon filtration and

washing, highly purified CA wetcake is recovered. This can be recycled to other processes to make additional quantities of TCCA, NaDCC or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

A further benefit of the method of the third embodiment of the invention is that it results in a liquid mixed halogen bromine and chlorine-containing composition that is safer and more convenient to produce than those that are predominantly bromine based.

A very surprising discovery of the invention is that the methods of the second and third embodiments use solid halogenating agents, instead of the liquid precursors used in the prior art, to prepare liquid bromine-containing compositions. The prior art methods use NaOCl solutions, Br<sub>2</sub>, or BrCl and describe chemistries that are designed to be accomplished under homogeneous, liquid phase conditions. The second and third embodiments are not performed under such conditions. Rather, they are performed under distinctly different, heterogeneous, solid-liquid conditions, because the solid halogenating agents never completely dissolve. The reaction chemistries of the second and third embodiments proceed rapidly, smoothly, and in high yield.

A further very surprising discovery of the present invention is that, using the method of the second embodiment, highly concentrated liquid bromine-containing compositions can be prepared under conditions of extremely high acidity. Indeed, the prior art teaches that such conditions are to be avoided in order to suppress undesirable hydrolysis of the sulfamic acid to ammonium sulfate. The presence of sulfate is undesirable because it is prone to precipitate and impair the physical stability of the solution. The presence of ammonium ion is undesirable as it reacts destructively with halogens to reduce the chemical yield of the reaction resulting in the formation of troublesome nitrogen gas bubbles in the reactor.

It is a further very surprising discovery of the present invention that the methods of the second and third embodiments use solid, organic halogenating agents instead of a NaOCl solutions, Br<sub>2</sub>, or BrCl to prepare aqueous bromine-containing compositions of far higher concentrations than previously reported. This is because solid, organic halogenating agents typically display only very limited water solubility, so it would be expected that the maximum concentration of a halogen-containing composition prepared using such materials would be correspondingly low. For example, trichloroisocyanuric acid dissolves in water to yield a saturated solution of just 1.1% as Cl<sub>2</sub> at 25° C. Nevertheless, the method of the present invention uses trichloroisocyanuric acid to prepare aqueous bromine-containing compositions having levels of halogen equivalent to almost 11% as Cl<sub>2</sub>.

Another advantage of this invention is that the fourth and fifth embodiments make possible the formation of a highly soluble bromine-containing solid composition using reagents that are more convenient to handle and less expensive to transport than alkali metal or earth alkali metal hypochlorite solutions.

The invention also has the advantage of using a single reactor sequence. In the methods of all of the embodiments, the complexing agent is introduced to the reaction as the free acid without the requisite for preforming its alkali metal or earth alkali metal salt in a separate reactor. Accordingly, since highly acidic conditions are maintained throughout the oxidation reactions, the possibility of bromate ion (an undesirable, carcinogenic by-product) being formed within the composition is eliminated.

Still another feature of the invention is that the fourth and fifth embodiments make possible the manufacture of a highly soluble bromine-containing solid composition in a process that neither employs nor generates measurable amounts of bromate.

Another advantage of this invention is that the methods of all of the embodiments make possible the formation of highly concentrated liquid or high-activity solid bromine-containing compositions in a series of fast, efficient, and high-yielding reactions.

This invention is also advantageous in that the methods of all of the embodiments make possible the formation of highly concentrated liquid or high-activity solid bromine-containing compositions using reagents that are safer, easier, and more convenient to handle and transport than the hazardous materials BrCl, elemental Br<sub>2</sub>, or gaseous Cl<sub>2</sub> utilized in the prior art processes.

## DETAILED DESCRIPTION OF THE INVENTION

### The First Embodiment

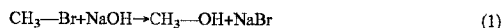
This embodiment is a method of preparing a highly concentrated aqueous bromine-containing biocide composition using anhydrous hydrogen bromide gas and a concentrated solution of hydrogen peroxide. The method preferably includes the following steps. Steps (a) and (b) may be performed in any order, or simultaneously, followed by step (c).

a. Mixing a complexing agent with a concentrated solution of hydrogen peroxide to form a slurry.

Preferably, the complexing agent is solid sulfamic acid and is introduced to the hydrogen peroxide solution with stirring. Hydrogen peroxide solution is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is recommended as it is safer to use and is more commonly available.

b. Introducing a source of covalently bonded anhydrous hydrogen bromide gas into the slurry.

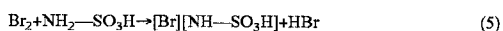
One source of anhydrous hydrogen bromide gas is the reaction medium in which bromide ion is released from an organobromine complex in a nucleophilic displacement reaction. An example would be the reaction of methyl bromide with sodium hydroxide (reaction 1) followed by acidification with mineral acid (reaction 2):



However, a preferred source of anhydrous hydrogen bromide gas is an emission from a reactor where bromination of an organic compound is taking place.



The hydrogen bromide gas is directed subsurface, and with agitation, to a reactor containing the slurry of sulfamic acid in strong hydrogen peroxide solution. The hydrogen peroxide oxidizes the hydrogen bromide gas to bromine as shown in reaction (4). Bromine reacts with sulfamic acid to form a bromo derivative and co-produce an additional amount of hydrogen bromide as illustrated by reaction (5).



## Recycle in (4)

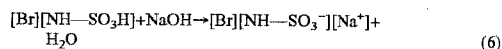
The amount of anhydrous hydrogen bromide gas added to the reactor is such that between 10% and 100% of the Br moieties form a complex with sulfamic acid. The amount of sulfamic acid present in the slurry depends on the amount of anhydrous hydrogen bromide introduced to the reactor. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid:hydrogen bromide is advantageous to the stability of the final product with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

The reaction time and temperature are controlled in order to maximize the conversion of hydrogen bromide gas into bromine, and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium. Processing can be performed in the batch or continuous mode. In continuous processing, the reactor size can be significantly reduced without loss in product output rate. The reactants are co-fed to a common junction as the reaction products are continuously withdrawn. In both continuous and batch processes, the reactions are conducted with mixing. The oxidation of hydrogen bromide gas with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction mixture using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor.

When hydrogen peroxide is used in this fashion, all of the Br moieties introduced to the reactor as hydrogen bromide materialize as active bromine in the final product. None are wasted as by-product bromide ion salts.

c. Adding an alkaline source to the reaction medium.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used in the process of this invention. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (6).



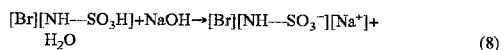
The amount of NaOH solution employed depends on its strength and on the initial charge of hydrogen bromide gas. The overall mole ratio of hydrogen bromide gas to NaOH is in the range of about 1:2 to about 1:5 and preferably about 1:3 to about 1:4.

## PROSPECTIVE EXAMPLE 1

Hydrogen bromide gas (8.09 g/min) is directed to a mixing unit for contact with a slurry formed by combining sulfamic acid (11.64 g/min) and 50% hydrogen peroxide (6.8 g/min). The overall reaction is:



The temperature and contact time are controlled so that the reaction is driven to completion and no unreacted  $\text{H}_2\text{O}_2$  remains in the reaction medium whereupon 50% NaOH (28.0 g/min) is introduced to complete the process according to reaction (8).



## The Second Embodiment

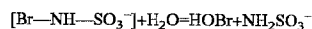
This embodiment is a method of preparing highly concentrated liquid bromine-containing compositions using an aqueous solution of bromide ions, a concentrated solution of hydrogen peroxide, and a solid halogenating agent (either organic or inorganic).

Overall, this method is advantageous in that it uses a high strength hydrogen peroxide solution in combination with a solid halogenating agent. This method results in a composition that contains significantly lower amounts of contaminant halide ion salts than solutions prepared using  $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{Cl}_2/\text{NaBr}$ , or  $\text{NaOCl}/\text{NaBr}$  solutions and is thus highly stable to chemical and physical decomposition processes. This stabilized composition possesses far higher bromine concentrations than those available from using  $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{Cl}_2$ , and even the strongest solutions of sodium hypochlorite. Thus, practice of this method provides a stable, aqueous composition of matter that contains 60–80% more available bromine than solutions that are currently commercially available. Moreover, the aqueous composition of this invention contains the highest concentration of bromine hitherto reported in the prior art. Typically, the composition of this invention contains greater than 21.4% as  $\text{Br}_2$  (9.4% as  $\text{Cl}_2$ ). It is golden yellow in color.

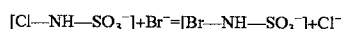
The method of this embodiment may also be used to prepare a liquid mixed halogen composition that contains both bromine and chlorine. The method uses a solution of bromide ions in conjunction with a molar excess of the combination of hydrogen peroxide and a solid chlorinating agent (either organic or inorganic). This light golden-colored composition contains 60–80% more available halogen than the all-bromine solutions that are currently available commercially. Typically, the mixed halogen composition prepared using this method contains a total halogen level of greater than 21% expressed as  $\text{Br}_2$  (9.4% expressed as  $\text{Cl}_2$ ).

A major benefit of a mixed halogen biocide is in the treatment of contaminated water that exerts a considerable halogen demand. This chemical demand can be satisfied by the less expensive chlorine portion of the composition, permitting more of the bromine portion to be available for microbiological control. Mixed halogen compositions are also safer and more convenient to manufacture than those that are predominantly bromine based. For example, during the preparation of the latter, the solutions have a tendency to emit deep red, highly corrosive and toxic bromine fumes right up until the final addition of the alkaline source. These vapors must be scrubbed from the reaction vessel's headspace in order to eliminate atmospheric release, worker exposure, and to prevent the fumes from entering and damaging expensive vacuum processing equipment. By contrast, the mixed halogen compositions emit hardly any deep red bromine fumes during their manufacture. Thus, the necessity for scrubbing the reaction vessel's headspace is eliminated.

A further significant aspect of compositions based on mixtures of stabilized bromine and chlorine is that in water systems employing long contact times, there may be sufficient time for the N-chlorosulfamate to react with "spent" bromide ion and regenerate N-bromosulfamate according to the following schematic.



Upon performing biocidal and oxidative reactions, HOBr reverts to soluble bromide ion. This can enter into reaction with N-chlorosulfamate to form additional N-bromosulfamate:



In this way, the consumer is able to derive the performance benefits of 2 moles of N-bromosulfamate for the price of 1 mole of N-bromosulfamate and 1 mole of N-chlorosulfamate.

As a general rule, chlorinated compounds display higher water solubility than their brominated counterparts. Further, a mixed halogen composition may be formulated to employ far less sodium bromide salt than an all-bromine solution. Thus, another highly advantageous facet of this invention is that it makes possible the formation of a mixed halogen composition that is lower in solids and is inherently more soluble than those based solely on bromine. This highly water-soluble composition exhibits improved physical stability as it becomes less prone to solid precipitation on storage.

#### 1. The Method of Preparing an All-Bromine Composition Using Hydrogen Peroxide

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by step (d).

a. Utilizing an aqueous solution of bromide ions in which the pH is less than +1.

The first step of this method is conducted under conditions of extreme acidity, preferably at a pH which is greater than -1 and less than +1. Any acidified source of bromide ions can be employed in the practice of this invention, for example, an aqueous solution of sodium bromide acidified with a strong mineral acid such as hydrochloric or nitric acid. However, aqueous hydrogen bromide is a preferred starting material and can be used at any concentration up to 70% by weight, although 48% is especially convenient to use as this is the concentration at which the product does not appreciably fume HBr vapors.

b. Introducing to the highly acidic solution of bromide ions, a highly concentrated solution of hydrogen peroxide to effect a partial or complete oxidation of the bromide ions into bromine.



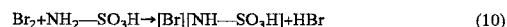
Strong solutions of hydrogen peroxide are preferably introduced to the 48% aqueous hydrogen bromide solution, although the order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is safer to use and is more commonly available. Preferably, 50% hydrogen peroxide is added slowly and with stirring to a solution of 48% aqueous hydrogen bromide calculated to have a pH of -0.78. The amount of 50% hydrogen peroxide added to the 48% aqueous hydrogen bromide solution should be sufficient to oxidize between 10% and 100% of the stoichiometric amount and, most preferably, between 20% and 80% of the stoichiometric amount of bromide ions into bromine. The oxidation of aqueous hydrogen bromide with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction medium using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of bromide into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

When hydrogen peroxide is used in this fashion, all of the Br moieties introduced to the reactor as hydrobromic acid can materialize as active bromine in the final product. None are wasted as by-product bromide ion salts. In this regard, hydrogen peroxide may also be used advantageously in reactions where elemental bromine is the starting raw material. Instead of wasting half of the Br moieties as inactive

bromide ion, regeneration by hydrogen peroxide as described in reactions (9) and (10) will ensure that both bromine atoms are utilized as active forms.

c. Mixing a complexing agent to the fully or partially oxidized solution.

On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the same reactor. Preferably the complexing agent is solid sulfamic acid. Bromine reacts with sulfamic acid to form a bromo-derivative and co-produces an additional amount of hydrogen bromide as illustrated by reaction (10).

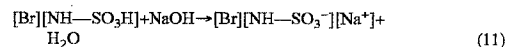


The amount of sulfamic acid added depends on the amount of aqueous hydrogen bromide originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to aqueous hydrogen bromide is advantageous to the stability of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

In the event that the reaction medium is 100% oxidized by hydrogen peroxide in step (b), the method concludes with step (d). However, even in the event that the reaction medium is only partially oxidized in step (b), the method concludes with step (d).

d. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous hydrogen bromide to hydroxide is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (14).



The amount of 50% NaOH solution employed depends on the initial charge of aqueous hydrogen bromide. The overall mole ratio of aqueous hydrogen bromide to NaOH added in steps (d) is in the range of about 1:2 and about 1:5, preferably about 1:3 to about 1:4.

#### 2. The Method of Preparing an All-Bromine Composition Using Hydrogen Peroxide and a Solid Organic Halogenating Agent

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by the remaining steps.

a. Utilizing an aqueous solution of bromide ions in which the pH is less than +1.

The first step of this method is conducted under conditions of extreme acidity, preferably at a pH which is greater than -1 and less than +1. Any acidified source of bromide ions can be employed in the practice of this invention, for example, an aqueous solution of sodium bromide acidified with a strong mineral acid such as hydrochloric or nitric acid. However, aqueous hydrogen bromide is a preferred starting material and can be used at any concentration up to 70% by weight, although 48% is especially convenient to

use as this is the concentration at which the product does not appreciably fume HBr vapors.

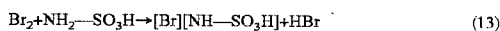
b. Introducing to the highly acidic solution of bromide ions, a highly concentrated solution of hydrogen peroxide to effect a partial or complete oxidation of the bromide ions into bromine.



Strong solutions of hydrogen peroxide are preferably introduced to the 48% aqueous hydrogen bromide solution, although the order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is safer to use and is more commonly available. Preferably, 50% hydrogen peroxide is added slowly and with stirring to a solution of 48% aqueous hydrogen bromide calculated to have a pH of -0.78. The amount of 50% hydrogen peroxide added to the 48% aqueous hydrogen bromide solution should be sufficient to oxidize between 10% and 100% of the stoichiometric amount and, most preferably, between 20% and 80% of the stoichiometric amount of bromide ions into bromine. The oxidation of aqueous hydrogen bromide with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction medium using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of bromide into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

c. Mixing a complexing agent to the fully or partially oxidized solution.

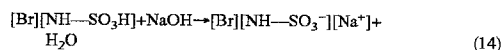
On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the same reactor. Preferably the complexing agent is solid sulfamic acid. Bromine reacts with sulfamic acid to form a bromo-derivative and co-produces an additional amount of hydrogen bromide as illustrated by reaction (13).



The amount of sulfamic acid added depends on the amount of aqueous hydrogen bromide originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to aqueous hydrogen bromide is advantageous to the stability of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

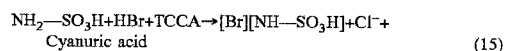
d. Adding an alkaline source to the reaction medium to adjust its pH to between about 0.5 and about 9 and preferably between about 1.0 and about 4.5.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (14).



e. Introducing sufficient solid, organic halogenating agent to oxidize all or substantially all of the remaining bromide ions into bromine.

Solid organic halogenating agents include any organic compound in which one or more halogen atoms such as Cl, Br, or I is present in oxidation state +1 and is covalently bound to a nitrogen or phosphorus atom within the same molecule. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichloroisocyanurate (NaDCC), sodium dichloroisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), potassium dichloroisocyanurate (KDCC), dichloroisocyanuric acid (DCCA), trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide. A particularly preferred source of a solid, organic halogenating agent is trichloroisocyanuric acid (TCCA), which reacts with aqueous hydrogen bromide and unreacted sulfamic acid according to the following equation.



Preferably TCCA is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the TCCA reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident. Although granular TCCA is favored because of its easy handling characteristics, and for providing a visual signal that the reaction is complete, TCCA powdered wetcake may also be employed. The advantage of using TCCA powdered wetcake is that it may be taken directly from the TCCA-producing reactors to eliminate costs associated with drying and granulation of the material.

f. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. When the solid organic halogenating agent is TCCA, cyanuric acid (CA) is a reaction by-product that is insoluble in the reaction medium (see reaction (15)). Filtration of the CA residue is carried out at pH 1-9, but preferably at pH 1.5-4.5 to maximize its recovery from solution and minimize the amount of bromine vapor that fumes from the reaction medium. Upon washing the filtercake with water to remove the mother liquors, a highly pure CA wetcake is recovered. This can be recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

If desired, this step can be modified so that the sodium salt of cyanuric acid is recovered from the reaction medium instead of cyanuric acid. This is accomplished by introducing, before performing the solid-liquid separation, sufficient 50% NaOH to react with cyanuric acid according to the following equation:



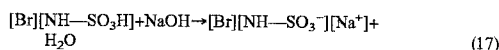
The amount of 50% sodium hydroxide solution employed depends on the amount of solid organic halogenating agent used in step (e) that is introduced to oxidize all or substantially all of the remaining bromide ions into bromine. When TCCA is the solid organic halogenating agent, sufficient



50% NaOH solution is introduced slowly with mixing and cooling to convert all or substantially all of the cyanuric acid liberated in equation (15) into its monosodium salt via reaction (16). Monosodium cyanurate is insoluble in the reaction medium at pH < 9. As is true of cyanuric acid, monosodium cyanurate can be separated and recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention. This is accomplished by performing a solid-liquid separation, as described above, which is done when the pH stabilizes at about 9.

g. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous hydrogen bromide to hydroxide is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (f).

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (17).



The amount of 50% NaOH solution employed depends on the initial charge of aqueous hydrogen bromide. The overall mole ratio of aqueous hydrogen bromide to NaOH added in steps (d) and (g) is in the range of about 1:2 and about 1:5, preferably about 1:3 to about 1:4. This does not include any 50% NaOH solution that may be used to convert cyanuric acid into its monosodium salt as described in step (f).

h. Removing any further insoluble residues that develop with a conventional solid-liquid separation technique.

As noted above, any suitable solid-liquid separation technique may be employed. Generally, when TCCA is the halogenating agent, almost 90% of CA reaction by-product is recovered as a highly pure wetcake in the first solid-liquid separation step described in step (f). While not wishing to be

bound by theory, it is believed that salts of cyanuric acid are precipitated from the reaction mother liquors upon the addition of alkaline sources. When the alkaline source is, for example, 50% sodium hydroxide solution, the mono-, di-, and trisodium salts of cyanuric acid are precipitated. Although insoluble in the reaction mother liquors, the di and trisodium salts display exceptional solubility in ordinary water and are thus useful water treating agents in their own right. However, in comparison to the amount of solids recovered in step (f), the amount of solid that may subsequently develop is relatively low and step (h) may require only a polishing solid-liquid separation, with, for example, a cartridge filter. Moreover, the two solid-liquid separation steps of (f) and (h) may be combined into a single operation performed only at step (f).

#### EXAMPLES 2-8

A general procedure for preparing the liquid stabilized bromine concentrates listed in Table II is as follows:

To a stirred reaction flask containing 48% hydrogen bromide (27.8 g) was added 50% H<sub>2</sub>O<sub>2</sub> (4.26 g) dropwise so that the reaction flask temperature did not exceed 142° F. After allowing the reaction flask to cool to around 95° F., solid sulfamic acid (19.2 g) was introduced. The resulting slurry was stirred as 50% sodium hydroxide solution was charged to the reaction flask to give a pH of between 1 and 10. The flask was chilled during this process so that the temperature did not exceed 80-90° F. A single charge of granular trichloroisocyanuric acid (8.81 g) was introduced to the reaction flask and stirred for 10-15 minutes or until all the coarse granules were observed to have reacted and a fine powdery precipitate developed. The solid was removed by vacuum filtration and the filter cake was washed with deionized water that was combined with the mother liquors. A second charge of 50% NaOH was then introduced also with cooling, and stirring at a rate such that the temperature did not exceed 80-90° F. Any additional precipitate that developed was immediately removed by vacuum filtration or the reaction flask was allowed to stand overnight and then filtered. In each case, the filter cake was washed with deionized water that was combined with the mother liquors. Iodometric titration of the resulting golden yellow solutions was used to determine the weight % Br<sub>2</sub> (or Cl<sub>2</sub>) contents. The theoretical amounts of Br<sub>2</sub> (or Cl<sub>2</sub> equivalent) produced as a function of the sum of the hydrogen peroxide and TCCA charges were then used to compute the % yield of each reaction.

TABLE II

Example	Initial 50% NaOH charge/g	pH before TCCA addition	Second 50% NaOH charge/g	Amount D.I. wash water to mother liquors	Final pH	Wt % as Br <sub>2</sub> (Cl <sub>2</sub> )	% Yield
2	22.0	NM	15.75	2 x 5 ml	12.4	23.5 (10.45)	87.0
3	22.0	1.5	14.95	1 x 5 ml	12.9	22.9 (10.2)	80.1
4	22.0	NM	31.2	2 x 5 ml	12.6	22.05 (9.8)	93.7
5	25.0	10.4*	20.0	2 x 5 ml	>12.5	24.36 (10.83)	96.5
6	22.4	3.3	20.5	1 x 5 ml	13.25	23.32 (9.92)	82.7



TABLE II-continued

Example	Initial 50% NaOH charge/g	pH before TCCA addition	Second 50% NaOH charge/g	Amount D.I. wash water to mother liquors	Final pH	Wt % as Br <sub>2</sub> (Cl <sub>2</sub> )	% Yield
7	20.4	NM	25.0	1 × 5 ml + 1 × 2 ml	13.0	22.36 (9.94)	86.5
8 <sup>a</sup>	20.5	NM	24.0	2 × 5 ml	12.93	21.96 (9.76)	88.4

\*prior to TCCA addition, the pH was readjusted to 2.4 by addition of a little sulfamic acid.

<sup>a</sup>the TCCA was substituted with 14.5 g sodium dichloroisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O) in this example.

NM denotes a parameter that was not measured.

## EXAMPLE 9

This example represents a four-fold scale-up of the reactions described in examples 2-8.

To a stirred reaction flask containing 48% hydrogen bromide (111.2 g) was added 50% H<sub>2</sub>O<sub>2</sub> (16.96 g) dropwise so that the reaction flask temperature did not exceed 142° F. After allowing the reaction flask to cool to around 85° F, solid sulfamic acid (76.8 g) was introduced. The resulting slurry was stirred as 50% sodium hydroxide solution (91.9 g) was charged to the reaction flask to give a pH of 1.5. The flask was chilled during this process so that the temperature did not exceed 80-90° F. A single charge of granular trichloroisocyanuric acid (TCCA) (36.0 g) was introduced to the reaction flask that was stirred for 20 minutes. Most of the coarse TCCA granules were observed to have reacted within this period, as a fine powdery precipitate developed and the pH of the reaction medium was measured to be 1.5. Deionized water (28 g) was added to the reaction flask to facilitate the complete reaction of the TCCA. The cyanuric acid solid was removed by vacuum filtration and the filter cake was washed with deionized water (12.5 ml) that was not combined with the mother liquors. The wet filter cake was placed in an oven at 130° F. for drying overnight. To the filtration mother liquors was added 50% NaOH (104 g), also with cooling, and at a rate such that the temperature did not exceed 80-90° F. Any additional solid cyanurate salts that developed were removed by vacuum filtration. The solids retained on the filter were washed with deionized water (5.0 g) and then dried in an oven at 130° F. Iodometric titration of the resultant golden yellow solution yielded a % Br<sub>2</sub> content of 23.7% (or 10.54% as Cl<sub>2</sub>). The theoretical amount of Br<sub>2</sub> (or Cl<sub>2</sub> equivalent) produced as a function of the sum of the hydrogen peroxide and TCCA charges was used to compute a reaction yield of 93.6%. The weight of the dried solids removed by filtration indicated that cyanuric acid and cyanurate salts were recovered in close to quantitative yield.

### 3. The Method of Preparing an All-Bromine Composition Using Hydrogen Peroxide and a Solid Inorganic Halogenating Agent

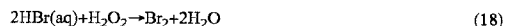
The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by the remaining steps.

a. Utilizing an aqueous solution of bromide ions in which the pH is less than +1.

The first step of this method is conducted under conditions of extreme acidity, preferably at a pH which is greater than -1 and less than +1. Any acidified source of bromide ions can be employed in the practice of this invention, for example, an aqueous solution of sodium bromide acidified

with a strong mineral acid such as hydrochloric or nitric acid. However, aqueous hydrogen bromide is a preferred starting material and can be used at any concentration up to about 70% by weight, although 48% is especially convenient to use, as this is the concentration at which the product does not appreciably fume HBr vapors.

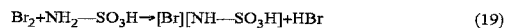
b. Introducing to the highly acidic solution of bromide ions, a highly concentrated solution of hydrogen peroxide to effect a partial or complete oxidation of the bromide ions into bromine.



Strong solutions of hydrogen peroxide are preferably introduced to the 48% aqueous hydrogen bromide solution, although the order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is safer to use and is more commonly available. Preferably, 50% hydrogen peroxide is added slowly and with agitation to a solution of 48% aqueous hydrogen bromide which has a pH -0.78. The amount of 50% hydrogen peroxide added to the 48% aqueous hydrogen bromide solution should be sufficient to oxidize between 10% and 100% of the stoichiometric amount, and most preferably between 20% and 80% of the stoichiometric amount of bromide ions into bromine. The oxidation of aqueous hydrogen bromide with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction mixture using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of bromide into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

c. Mixing a complexing agent to the fully or partially oxidized solution.

On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the same reactor. Preferably the complexing agent is solid sulfamic acid. Bromine reacts with sulfamic acid to form a bromo-derivative and co-produces an additional amount of hydrogen bromide as illustrated by reaction (19).

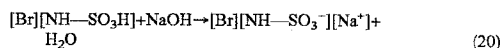


The amount of sulfamic acid added depends on the amount of aqueous hydrogen bromide originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to aqueous hydrogen bromide is advantageous to the stability

of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

d. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous hydrogen bromide to hydroxide is between about 0.5:1 and about 1:2, preferably between about 1:1.

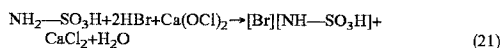
Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (20).



e. Introducing sufficient solid, inorganic halogenating agent to oxidize all or substantially all of the remaining bromide ions into bromine.

Solid inorganic halogenating agents include, but are not limited to, alkali metal and earth alkali metal hypochlorite salts. Suitable examples include lithium hypochlorite, calcium hypochlorite, and magnesium hypochlorite. Due to its low cost and high available chlorine content, calcium hypochlorite is particularly preferred. The higher strength granular forms of the product (containing 65–75% available chlorine) are most preferred.

Under such strongly acidic conditions (pH between about –1 and about 5), the oxidation reaction written at reaction (21) is virtually instantaneous and proceeds to completion in a short time.



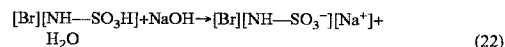
The calcium hypochlorite is preferably added to the reactor rapidly and with good mixing in order to minimize loss of bromine vapors from the reaction medium but not too quickly such that phase separation of elemental bromine becomes apparent at the bottom of the reactor. The granular form of solid calcium hypochlorite facilitates the transfer of the product into the reaction vessel. As it reacts, the coarse granules disappear, and the reaction is considered to be complete when no more coarse granules are evident. When this occurs, all the sulfamic acid has reacted to yield a bromo-sulfamic acid complex.

f. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. When the solid inorganic halogenating agent is calcium hypochlorite, insoluble reaction by-products include calcium carbonate, lime, and quicklime. Filtration of the reaction medium is carried out at pH 1–9, but preferably at about pH 4–8 to mitigate the problem of CO<sub>2</sub> gas being liberated from calcium carbonate and also minimize the amount of bromine vapor that is emitted from the reaction medium.

g. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous hydrogen bromide to hydroxide is between about 1:2 and about 1:4, preferably between about 1:3 and about 1:4.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (22).



The amount of 50% NaOH solution employed depends on the initial charge of aqueous hydrogen bromide. The overall mole ratio of aqueous hydrogen bromide to NaOH added in steps (d) and (g) is in the range of about 1:2 to about 1:4, preferably about 1:3 to about 1:4.

#### EXAMPLES 10–11

A general procedure for preparing the liquid stabilized bromine concentrates listed in Table III is as follows:

To a stirred reaction flask containing 48% HBr, the appropriate amount of 50% hydrogen peroxide was added drop-wise at a rate such that the temperature did not exceed 142° F. After allowing the reaction flask to cool to around 95° F., solid sulfamic acid was introduced. The resulting slurry was stirred as the appropriate amount of 50% NaOH solution was charged to the reaction flask that was cooled so the temperature did not exceed 85° F. Thereafter, the correct amount of granular calcium hypochlorite (59.5% available chlorine) was introduced, also with stirring. Upon filtration of insolubles, sufficient 50% NaOH and solid NaOH was slowly introduced so that the overall mole ratio of aqueous hydrogen bromide to hydroxide was 1:3. During the addition, the reaction flask was cooled on ice so that the temperature of the contents did not exceed 80–90° F. Iodometric titration of the resultant golden yellow solutions was used to determine the weight % Br<sub>2</sub> (or Cl<sub>2</sub>) contents. The theoretical amounts of Br<sub>2</sub> (or Cl<sub>2</sub> equivalent) produced as a function of the sum of the hydrogen peroxide and calcium hypochlorite charges were then used to compute the % yield of each reaction.

TABLE III

Ex- am- ple	Mass 50% H <sub>2</sub> O <sub>2</sub> /g	Mass 48% HBr/ g	Mass sulfamic acid/g	Mass Ca(OCl) <sub>2</sub> (59.5% av. Cl <sub>2</sub> )/g	Mass NaOH/g (1) 1 <sup>st</sup> (2) 2 <sup>nd</sup>	Wt. % as Br <sub>2</sub> (Cl <sub>2</sub> )	% Yield
10	4.22	27.82	19.2	11.0	(1) 13 g 50% (2) 10 g 50% + 10 g 100%	21.6 (9.6)	83.5
11	8.48	55.6	38.4	24.22	(1) 26 g 50%	21.3 (9.48)	70.8

TABLE III-continued

Ex- am- ple	Mass 50% H <sub>2</sub> O <sub>2</sub> /g	Mass 48% HBr/ g	Mass sulfamic acid/g	Mass Ca(OCl) <sub>2</sub> (59.5% av. Cl <sub>2</sub> )/g	Mass NaOH/g (1) 1 <sup>st</sup> (2) 2 <sup>nd</sup>	Wt. % as Br <sub>2</sub> (Cl <sub>2</sub> )	Yield %
					(2) 8 g 50% + 13 g 100%		

#### 4. The Method of Preparing a Mixed Halogen Composition Using a Solid Organic Chlorinating Agent

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by the remaining steps.

a. Utilizing an aqueous solution of bromide ions in which the pH is less than +1.

The first step of this method is conducted under conditions of extreme acidity, preferably at a pH which is greater than -1 and less than +1. Any acidified source of bromide ions can be employed in the practice of this invention, for example, an aqueous solution of sodium bromide acidified with a strong mineral acid such as hydrochloric or nitric acid. However, aqueous hydrogen bromide is a preferred starting material and can be used at any concentration up to 70% by weight, although 48% is especially convenient to use as this is the concentration at which the product does not appreciably fume HBr vapors.

b. Introducing to the highly acidic solution of bromide ions, a highly concentrated solution of hydrogen peroxide to effect a partial or complete oxidation of the bromide ions into bromine.



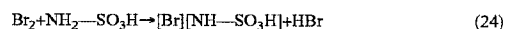
Strong solutions of hydrogen peroxide are preferably introduced to the 48% aqueous hydrogen bromide solution, although the order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is safer to use and is more commonly available. Preferably, 50% hydrogen peroxide is added slowly and with stirring to a solution of 48% aqueous hydrogen bromide calculated to have a pH of -0.78. The amount of 50% hydrogen peroxide added to the 48% aqueous hydrogen bromide solution should be sufficient to oxidize between 10% and 100% of the stoichiometric amount and, most preferably, between 20% and 80% of the stoichiometric amount of bromide ions into bromine. The oxidation of aqueous hydrogen bromide with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction medium using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of bromide into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

When hydrogen peroxide is used in this fashion, all of the Br moieties introduced to the reactor as hydrobromic acid materialize as active bromine in the final product. None are wasted as by-product bromide ion salts.

c. Mixing a complexing agent to the fully or partially oxidized solution.

On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the

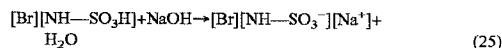
same reactor. Preferably the complexing agent is solid sulfamic acid. Bromine reacts with sulfamic acid to form a bromo-derivative and co-produces an additional amount of hydrogen bromide as illustrated by reaction (24).



The amount of sulfamic acid added depends on the amount total halogen required in the final product. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to total halogen is advantageous to the stability of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

d. Adding an alkaline source to the reaction medium to adjust its pH to between about 0.5 and about 9 and preferably between about 1.0 and about 4.5.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (25).

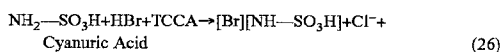


e. Introducing sufficient solid, organic chlorinating agent to complete the oxidation of the bromide ions into bromine (if the solution is only partially oxidized in step (b)), and to release soluble chlorine into the solution by complexing with sulfamic acid.

The molar equivalent of the combination of hydrogen peroxide added in step (b) and solid chlorinating agent should be in excess of the molar equivalent of bromide ions added in step (a). Employing a 10% molar excess of the combination of hydrogen peroxide and solid organic chlorinating agent over the bromide ions, yields a mixed halogen composition of 90 mole % bromine and 10 mole % chlorine.

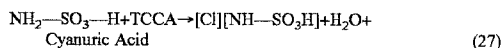
Solid organic chlorinating agents include any organic compound in which the chlorine atom is in oxidation state +1 and is covalently bound to a nitrogen or phosphorus atom within the same molecule. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichloroisocyanurate (NaDCC), sodium dichloroisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), potassium dichloroisocyanurate (KDCC), dichloroisocyanuric acid (DCCA), trichloromelamine,

N-chloro-p-toluenesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin. A particularly preferred source of a solid, organic chlorinating agent is trichloroisocyanuric acid (TCCA). In completing the oxidation of hydrogen bromide solution, TCCA reacts according to the following equation.



23

In releasing soluble chlorine into the aqueous solution by complexing with sulfamic acid, it reacts according to equation (27).



Preferably TCCA is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the TCCA reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident. Although granular TCCA is favored because of its easy handling characteristics, and for providing a visual signal that the reaction is complete, TCCA powdered wetcake may also be employed. The advantage of using TCCA powdered wetcake is that it may be taken directly from the TCCA-producing reactors to eliminate costs associated with drying and granulation of the material.

f. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. When the solid organic chlorinating agent is TCCA, cyanuric acid (CA) is a reaction by-product that is insoluble in the reaction medium (see reactions (26) and (27)). Filtration of the cyanuric acid residue is carried out at pH 1–9, but preferably at pH 1.5–4.5 to maximize CA recovery from solution and minimize the amount of bromine vapor that fumes from the reaction medium. Upon washing the filtercake with water to remove the mother liquors, a highly pure CA wetcake is recovered. This can be recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

If desired, this step can be modified so that the sodium salt of cyanuric acid is recovered from the reaction medium instead of cyanuric acid. This is accomplished by introducing, before performing the solid-liquid separation, sufficient 50% NaOH to react with cyanuric acid according to the following equation:



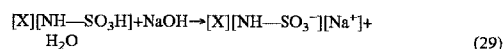
The amount of 50% sodium hydroxide solution employed depends on the amount of solid organic chlorinating agent used in step (e) that is introduced to oxidize all or substantially all of the remaining bromide ions into bromine, and to release soluble chlorine into the aqueous solution by complexing with sulfamic acid. When TCCA is the solid organic chlorinating agent, sufficient 50% NaOH solution is introduced slowly with mixing and cooling to convert all or substantially all of the cyanuric acid liberated in reactions (26) and (27) into its monosodium salt via reaction (28). Monosodium cyanurate is insoluble in the reaction medium at pH < 9. As is true of cyanuric acid, monosodium cyanurate can be separated and recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention. This is accompanied by performing a solid-liquid separation, as described above, which is done when the pH stabilizes at about 9.

g. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the mole ratio of chlorine that is equivalent to the combination

24

of hydrogen peroxide and solid organic chlorinating agent to the hydroxide added in steps (d) and (g) is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (f).

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the halo derivatives of sulfamic acid to form the halo derivatives of sodium sulfamate according to reaction (29).



X=Br and Cl

The amount of 50% NaOH solution depends on the amount of hydrogen peroxide and solid organic chlorinating agent employed. The overall mole ratio of chlorine that is equivalent to the combination of hydrogen peroxide and solid organic chlorinating agent to the hydroxide added in steps (d) and (g) is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4. This does not include any 50% NaOH solution that may be used to convert cyanuric acid into its monosodium salt as described in step (f).

h. Removing any further insoluble residues that develop with a conventional solid-liquid separation technique.

As noted above, any suitable solid-liquid separation technique may be employed. Generally, when TCCA is the chlorinating agent, almost 90% of CA reaction by-product is recovered as a highly pure wetcake in the first solid-liquid separation described in step (f). While not wishing to be bound by theory, it is believed that salts of cyanuric acid are precipitated from the reaction mother liquors upon the addition of alkaline sources. When the alkaline source is, for example, 50% sodium hydroxide solution, the mono-, di-, and trisodium salts of cyanuric acid are precipitated. Although insoluble in the reaction mother liquors, the di and trisodium salts display exceptional solubility in ordinary water and are thus useful water treating agents in their own right. However, in comparison to the amount of solids recovered in step (f), the amount of solid that may subsequently develop is relatively low and step (h) may require only a polishing solid-liquid separation, with, for example, a cartridge filter. Moreover, the two solid-liquid separation steps of (f) and (h) may be combined into a single operation performed only at step (f).

5. The Method of Preparing a Mixed Halogen Composition Using a Solid Inorganic Chlorinating Agent

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by the remaining steps.

a. Utilizing an aqueous solution of bromide ions in which the pH is less than +1.

The first step of this method is conducted under conditions of extreme acidity, preferably at a pH which is greater than -1 and less than +1. Any acidified source of bromide ions can be employed in the practice of this invention, for

25

example, an aqueous solution of sodium bromide acidified with a strong mineral acid such as hydrochloric or nitric acid. However, aqueous hydrogen bromide is a preferred starting material and can be used at any concentration up to 70% by weight, although 48% is especially convenient to use as this is the concentration at which the product does not appreciably fume HBr vapors.

b. Introducing to the highly acidic solution of bromide ions, a highly concentrated solution of hydrogen peroxide to effect a partial or complete oxidation of the bromide ions into bromine.

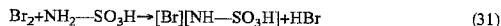


Strong solutions of hydrogen peroxide are preferably introduced to the 48% aqueous hydrogen bromide solution, although the order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, but 50% hydrogen peroxide is safer to use and is more commonly available. Preferably, 50% hydrogen peroxide is added slowly and with stirring to a solution of 48% aqueous hydrogen bromide calculated to have a pH of  $\sim 0.78$ . The amount of 50% hydrogen peroxide added to the 48% aqueous hydrogen bromide solution should be sufficient to oxidize between 10% and 100% of the stoichiometric amount and, most preferably, between 20% and 80% of the stoichiometric amount of bromide ions into bromine. The oxidation of aqueous hydrogen bromide with hydrogen peroxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction medium using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of bromide into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

When hydrogen peroxide is used in this fashion, all of the Br moieties introduced to the reactor as hydrobromic acid can materialize as active bromine in the final product. None are wasted as by-product bromide ion salts.

c. Mixing a complexing agent to the fully or partially oxidized solution.

On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the same reactor. Preferably the complexing agent is solid sulfamic acid. Bromine reacts with sulfamic acid to form a bromo-derivative and co-produces an additional amount of hydrogen bromide as illustrated by reaction (31).



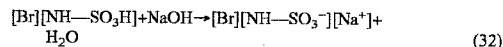
The amount of sulfamic acid added depends on the amount total halogen required in the final product. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to total halogen is advantageous to the stability of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

d. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous hydrogen bromide to hydroxide is between about 0.5:1 and about 1:2, preferably about 1:1.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alka-

26

line source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (32).

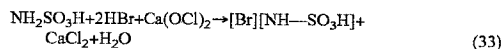


e. Introducing sufficient solid, inorganic chlorinating agent to complete the oxidation of the bromide ions into bromine (if the solution is only partially oxidized in step (b)), and to release soluble chlorine into the solution by complexing with sulfamic acid.

The molar equivalent of the combination of hydrogen peroxide added in step (b) and solid chlorinating agent should be in excess of the molar equivalent of bromide ions added in step (a). Employing a 10% molar excess of the combination of hydrogen peroxide and solid inorganic chlorinating agent over the bromide ions, yields a mixed halogen composition of 90 mole % bromine and 10 mole % chlorine.

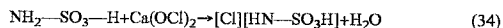
Solid inorganic chlorinating agents include, but are not limited to, alkali metal and earth alkali metal hypochlorite salts. Suitable examples include lithium hypochlorite, calcium hypochlorite, and magnesium hypochlorite. Due to its low cost and high available chlorine content, calcium hypochlorite is particularly preferred. The higher strength granular forms of the product (containing 65–75% available chlorine) are most preferred.

In completing the oxidation of hydrogen bromide solution,  $\text{Ca}(\text{OCl})_2$  reacts according to the following equation.



Under such strongly acidic conditions (pH between about  $-1$  and about  $5$ ), the oxidation reaction written at reaction (33) is virtually instantaneous and proceeds to completion in a short time.

In releasing soluble chlorine into the aqueous solution by complexing with sulfamic acid, calcium hypochlorite reacts according to equation (34).



The calcium hypochlorite is preferably added to the reactor rapidly and with good mixing in order to minimize loss of bromine vapors from the reaction medium but not too quickly such that phase separation of elemental bromine becomes apparent at the bottom of the reactor. The granular form of solid calcium hypochlorite facilitates the transfer of the product into the reaction vessel. As it reacts, the coarse granules disappear, and the reaction is considered to be complete when no more coarse granules are evident. When this occurs, all the sulfamic acid has reacted to yield mixed halogen-sulfamic acid complexes.

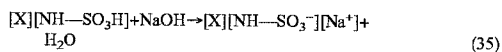
f. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. When the solid inorganic chlorinating agent is calcium hypochlorite, insoluble reaction by-products include calcium carbonate, lime, and quicklime. Filtration of the reaction medium is carried out at pH  $1-9$ , but preferably at about pH  $4-8$  to

mitigate the problem of CO<sub>2</sub> gas being liberated from calcium carbonate and also minimize the amount of bromine vapor that is emitted from the reaction medium.

g. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the mole ratio of chlorine that is equivalent to the combination of hydrogen peroxide and solid inorganic chlorinating agent to the hydroxide added in steps (d) and (g) is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the halo derivatives of sulfamic acid to form the halo derivatives of sodium sulfamate according to reaction (35).



X=Br and Cl

### The Third Embodiment

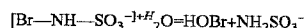
This embodiment is a method of preparing a concentrated liquid bromine-containing biocide composition using a solution of bromide ions and a solid halogenating agent (either organic or inorganic). This golden-colored composition contains 60-80% more available bromine than solutions that are currently available commercially. Moreover, the aqueous composition contains the highest concentration of bromine hitherto reported in the prior art. Typically, the composition of this invention contains greater than 18% as Br<sub>2</sub> (8% as Cl<sub>2</sub>).

This method of this embodiment may also be used to prepare a liquid mixed halogen composition that contains both bromine and chlorine. The method uses a source of bromide ions in conjunction with a molar excess of a solid chlorinating agent (either organic or inorganic). This light golden-colored composition contains 60-80% more available halogen than the all-bromine solutions that are currently available commercially. Typically, the mixed halogen composition prepared using this method contains a total halogen level of greater than 9.4% expressed as Cl<sub>2</sub> (21% expressed as Br<sub>2</sub>).

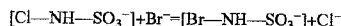
A major benefit of a mixed halogen biocide is in the treatment of contaminated water that exerts a considerable halogen demand. This chemical demand can be satisfied by the less expensive chlorine portion of the composition, permitting more of the bromine portion to be available for microbiological control. Mixed halogen compositions are also safer and more convenient to manufacture than those that are predominantly bromine based. For example, during the preparation of the latter, the solutions have a tendency to emit deep red, highly corrosive and toxic bromine fumes right up until the final addition of the alkaline source. These vapors must be scrubbed from the reaction vessel's headspace in order to eliminate atmospheric release, worker exposure, and to prevent the fumes from entering and damaging expensive vacuum processing equipment. By

contrast, the mixed halogen compositions emit hardly any deep red bromine fumes during their manufacture. Thus, the necessity for scrubbing the reaction vessel's headspace is eliminated.

A further significant aspect of compositions based on mixtures of stabilized bromine and chlorine is that in water systems employing long contact times, there may be sufficient time for the N-chlorosulfamate to react with "spent" bromide ion and regenerate N-bromosulfamate according to the following schematic.



Upon performing biocidal and oxidative reactions, HOBr reverts to soluble bromide ion. This can enter into reaction with N-chlorosulfamate to generate additional N-bromosulfamate



In this way, the consumer is able to derive the performance benefits of 2 moles of N-bromosulfamate for the price of 1 mole of N-bromosulfamate and 1 mole of N-chlorosulfamate.

As a general rule, chlorinated compounds display higher water solubility than their brominated counterparts. Further, a mixed halogen composition may be formulated to employ far less sodium bromide salt than an all-bromine solution. Thus, another highly advantageous facet of this invention is that it makes possible the formation of a mixed halogen composition that is lower in solids and is inherently more soluble than those based solely on bromine. This highly water-soluble composition exhibits improved physical stability as it becomes less prone to solid precipitation on storage.

The method preferably includes the following steps. Steps (a), (b), and (c) or steps (a), (b), and (d) may be performed in any order, or simultaneously, followed by the remaining steps.

a. Utilizing an alkali metal or earth alkali metal solution of bromide ions.

Sources of alkali metal or earth alkali metal solutions of bromide ions include, but are not limited to, lithium bromide, sodium bromide, potassium bromide, calcium bromide, and magnesium bromide. A preferred source of bromide ion solution is sodium bromide solution, commonly available as a 40-46% aqueous solution, or it may be made into such a solution by dissolving solid sodium bromide salt in water.

b. Mixing a complexing agent to the bromide ion solution.

Preferably the complexing agent is sulfamic acid. The amount of sulfamic acid added depends on the amount of bromide ion originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to sodium is advantageous to the stability of the final product with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

The next step is either (c) or (d).

c. Adding an alkaline source to the reaction medium to adjust its pH to between about 0.5 and about 9 and preferably between about 1.0 and about 4.5, followed by introducing sufficient solid, organic halogenating agent to oxidize all or substantially all of the bromide ions into bromine.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alka-

line source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F.

Solid organic halogenating agents include any organic compound in which one or more halogen atoms such as Cl, Br, or I is present in oxidation state +1 and is covalently bound to a nitrogen or phosphorus atom within the same molecule. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichlorisocyanurate (NaDCC), sodium dichlorisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide. A particularly preferred source of a solid, organic halogenating agent is trichloroisocyanuric acid (TCCA). Preferably this is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the TCCA reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident. Although dry, granular TCCA is favored because of its easy handling characteristics, and for providing a visual signal that the reaction is complete, TCCA powdered wetcake may also be employed. The advantage of using TCCA wetcake is that it may be taken directly from the TCCA-producing reactors and so costs associated with drying and granulation of the material are eliminated.



In order to prepare a mixed halogen solution, a molar excess of organic chlorinating agent to bromide ions is employed. Employing a 10% molar excess of the solid organic chlorinating agent over the bromide ions, yields a mixed halogen composition of 90 mole % bromine and 10 mole % chlorine. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichlorisocyanurate (NaDCC), sodium dichlorisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin. In this case, the organic chlorinating agent has dual functionality. First, it oxidizes all of the bromide ions into bromine which reacts with the sulfamic acid to form N-bromosulfamic acid as indicated in reaction (36). Second, the excess chlorinating agent releases soluble chlorine into the aqueous solution by complexing with sulfamic acid to form N-chlorosulfamic acid according to reaction (37).



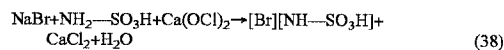
If step (c) is used, step (d) is not used. If step (c) is not used, step (d) is used.

d. Introducing sufficient solid inorganic halogenating agent to oxidize all or substantially all of the bromide ions into bromine.

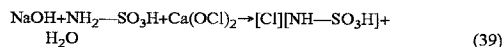
Solid inorganic halogenating agents include, but are not limited to, alkali metal and earth alkali metal hypochlorite salts. Suitable examples include lithium hypochlorite, calcium hypochlorite, and magnesium hypochlorite. Due to its

low cost and high available chlorine content, calcium hypochlorite is particularly preferred. The higher strength granular forms of the product (containing 65–75% available chlorine) are most preferred.

Under acidic conditions (pH between about –1 and about 5), the oxidation reaction is virtually instantaneous, and proceeds to completion in a short time. The calcium hypochlorite is preferably added rapidly and with good mixing in order to minimize loss of bromine vapors from the reaction mixture but not too quickly such that that phase separation of elemental bromine becomes apparent at the bottom of the reactor. When the addition of the calcium hypochlorite is complete, all the sulfamic acid has solubilized to yield an acidic reaction mixture. Preferably it is used in the form of a coarse granular grade for ease of introduction to the stirred, cooled reactor. As the calcium hypochlorite reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident.



In order to prepare a mixed halogen solution, a molar excess of inorganic chlorinating agent to bromide ions is employed. Employing a 10% molar excess of the solid inorganic chlorinating agent over the bromide ions, yields a mixed halogen composition of 90 mole % bromine and 10 mole % chlorine. Suitable examples include lithium hypochlorite, calcium hypochlorite, and magnesium hypochlorite. In this case, the inorganic chlorinating agent has dual functionality. First, it oxidizes all of the bromide ions into bromine which reacts with the sulfamic acid to form N-bromosulfamic acid as indicated in reaction (38). Second, the excess chlorinating agent releases soluble chlorine into the aqueous solution by complexing with sulfamic acid to form N-chlorosulfamic acid according to reaction (39).

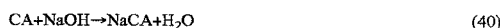


e. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation.

When the solid organic halogenating agent is TCCA, cyanuric acid is a reaction by-product that is insoluble in the reaction medium (see reactions (36) and (37)). Filtration of the cyanuric acid (CA) residue is carried out at pH 1–9, but preferably at pH 1–6 to maximize its recovery from solution and minimize the amount of bromine vapors that fume from the reaction medium. Upon washing the filtercake with water to remove the mother liquors, a highly pure CA wetcake is recovered. This can be recycled to other processes to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

If desired, this step can be modified so that the sodium salt of cyanuric acid is recovered from the reaction medium instead of cyanuric acid. This is accomplished by introducing, before performing the solid-liquid separation, sufficient 50% NaOH to react with cyanuric acid according to the following equation:



The amount of 50% sodium hydroxide solution employed depends on the amount of solid organic halogenating or chlorinating agent used in step (c). When TCCA is the solid organic halogenating or chlorinating agent, sufficient 50% NaOH solution is introduced slowly with mixing and cooling to convert all or substantially all of the cyanuric acid liberated in equations (36) and (37) into its monosodium salt via reaction (40). Monosodium cyanurate is insoluble in the reaction medium at pH<9. As is true of cyanuric acid, monosodium cyanurate can be separated and recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention. This is accomplished by performing a solid-liquid separation, as described above, which is done when the pH stabilizes at about 9.

When the solid inorganic halogenating agent is calcium hypochlorite, insoluble reaction by-products include calcium carbonate, lime, and quicklime. Filtration of the reaction medium is carried out at pH 1-9, but preferably at pH 4-8 to mitigate the problem of CO<sub>2</sub> gas being liberated from calcium carbonate and also minimize the amount of bromine vapors that fume from the reaction medium.

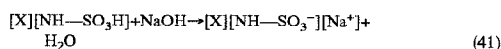
f. Adding an alkaline source to the reaction mother liquors.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F.

To prepare the all-bromine-containing liquid composition, and if the alkaline source is a hydroxide salt, the overall mole ratio of bromide ion to hydroxide added in steps (c) (if used) and (f) is between about 1:2 and about 1:4, preferably between about 1:3 and about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (e).

To prepare the liquid mixed halogen composition, and if the alkaline source is a hydroxide salt, the overall mole ratio of chlorine equivalent to hydroxide added in steps (c) (if used) and (f) is between about 1:2 and about 1:4, preferably between about 1:3 and about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (e).

In either case, the purpose is to deprotonate the halo derivatives of sulfamic acid to form the halo derivatives of sodium sulfamate according to reaction (41).



X=Br and Cl

g. Removing any further insoluble residues that develop with a conventional solid-liquid separation technique.

As noted above, any suitable solid-liquid separation technique may be employed. Generally, when TCCA is the halogenating agent, almost 90% of CA reaction by-product is recovered as a highly pure wetcake in the first solid-liquid separation operation described in step (e). While not wishing to be bound by theory, it is believed that salts of cyanuric

acid are precipitated from the reaction mother liquors upon the addition of alkaline sources. When the alkaline source is, for example, 50% sodium hydroxide solution, the mono-, di-, and trisodium salts of cyanuric acid are precipitated. Although insoluble in the reaction mother liquors, the di and trisodium salts display exceptional solubility in ordinary water and are thus useful water treating agents in their own right. However, in comparison to the amount of solids recovered in step (e), the amount of solid that may subsequently develop is relatively low and step (g) may require only a polishing solid-liquid separation, with, for example, a cartridge filter. Moreover, the two solid-liquid separation steps of (e) and (g) may be combined into a single operation performed only at step (e).

#### EXAMPLES 12-13

A general procedure for preparing the liquid stabilized bromine concentrates listed in Table IV is as follows:

To a stirred reaction flask containing 40% NaBr (25.7 g) was added deionized water (30 g) and solid sulfamic acid (11.7 g). The resulting slurry was stirred as 50% sodium hydroxide solution (9.65 g) was charged to the reaction flask to give a pH of 2.0. The flask was chilled during this process so that the temperature did not exceed 80-90° F. A single charge of granular trichlorocyanuric acid (7.74 g) was then introduced to the reaction flask.

In an alternate process, the step of introducing 50% sodium hydroxide was omitted, and calcium hypochlorite (10.67 g) was added to the reaction flask in place of TCCA. Within 15-30 minutes, fine powdery precipitates had developed in both cases. The solids were removed by vacuum filtration and the filter cakes were washed with copious amounts of deionized water to remove reaction mother liquors and dissolved salts. Then the appropriate amount of 50% NaOH solution was introduced to the filtered solution with cooling, and at a rate such that the temperature did not exceed 80-90° F. Any additional residues that developed were also removed by vacuum filtration. Iodometric titration of the resultant golden yellow solutions was used to determine their bromine content. The respective yields were calculated using the weight and assay of TCCA or Ca(OCl)<sub>2</sub> used in the initial charge to the reaction flask. Table IV summarizes the data obtained.

TABLE IV

Exam- ple	Reactant	Reactant assay/% as av. Cl <sub>2</sub>	Initial 50% NaOH charge/g	Final 50% NaOH charge/g	Wt. % Br <sub>2</sub> Cl <sub>2</sub>	% Yield
12	TCCA	90	9.65	10.0	14.76 (6.56)	85.0
13	Ca(OCl) <sub>2</sub>	59.5	0	22.0	14.4 (6.4)	100.9

\*From the weight of the dry filter cake, it was calculated that 88.5% of the cyanuric acid (CA) charged to the reaction flask as TCCA was recovered in the first filtration.

#### EXAMPLE 14

This example represents a scale-up of the reaction described in example 12.

To a stirred reaction flask containing 40% NaBr solution (182 g) was added deionized water (40 g) and solid sulfamic acid (82.4 g). The reaction medium was stirred and cooled as 50% sodium hydroxide solution (60.2 g) was slowly



introduced such that the temperature did not exceed 85° F. A single charge of granular trichloroisocyanuric acid (55 g) was then added to the reaction flask that was stirred for around 20 minutes. All of the coarse TCCA granules were observed to have reacted within this period as a fine powdery precipitate developed. Prior to filtration, the pH of the reaction liquors was adjusted to 1.55 by addition of more 50% NaOH solution (5.0 g). Upon filtration of the insolubles, the filtercake was washed with two bed volumes of deionized water. The wash liquors were discarded, and the filter wetcake was placed in an oven to dry overnight at 130° F. To the filtrate was added additional 50% NaOH (90 g) again with cooling and stirring and at a rate such that the temperature of the reaction did not exceed 80–90° F. Any additional solids that precipitated from solution were removed by vacuum filtration, immediately upon completing the addition of the 50% NaOH. Iodometric titration of the resultant golden solution yielded a Br<sub>2</sub> content of 22.7% (or 10.1% as Cl<sub>2</sub>). The theoretical amount of Br<sub>2</sub> (or Cl<sub>2</sub> equivalent) produced as a function of the amount of TCCA charged was used to compute a reaction yield of 98.8%. The weight of the dry solids removed on the first filtration indicated that 86.6% of the cyanuric acid had been recovered.

#### EXAMPLE 15

This example describes the preparation of a mixed halogen composition that contains both bromine and chlorine. The same conditions as those listed in Example 14 are employed except for using half the amount of NaBr.

To a stirred reaction flask containing 40% NaBr solution (91 g) was added deionized water (131 g) and solid sulfamic acid (82.4 g). The reaction medium was stirred and cooled as 50% sodium hydroxide solution (60.2 g) was slowly introduced such that the temperature did not exceed 85° F. A single charge of granular trichloroisocyanuric acid (55 g) was then added to the reaction flask. Shortly after half of the TCCA was added, the bromine fumes in the flask were observed to subside. Compared to the process employing twice as much NaBr there were virtually no bromine vapors evident. It was not necessary to quell the fumes by addition of 50% NaOH prior to filtration. After about 20 minutes of stirring, all of the coarse TCCA granules were observed to have reacted as a fine powdery precipitate developed. Upon filtration of the insolubles, the filtercake was washed with 2 bed volumes of deionized water. The wash liquors were discarded, and the filter wetcake was placed in an oven to dry overnight at 130° F. To the filtrate was added additional 50% NaOH (95 g) again with cooling and stirring, and at a rate such that the temperature of the reaction did not exceed 80–90° F. Any additional solids that precipitated from solution were removed by vacuum filtration, immediately upon completing the addition of the 50% NaOH. Iodometric titration of the resultant golden solution yielded a total halogen content of 21.1% when expressed as Br<sub>2</sub> (or 9.4% when expressed as Cl<sub>2</sub>). The theoretical amount of Br<sub>2</sub> and Cl<sub>2</sub> equivalent produced as a function of the amount of the TCCA charge was used to compute a reaction yield of 92.0%.

#### The Fourth Embodiment

This embodiment is a method of preparing heretofore unknown, highly water soluble, bromine-containing solid compositions of matter, namely, the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate and the

alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate. The method uses anhydrous hydrogen bromide or aqueous hydrogen bromide precursors under reaction conditions designed to promote the formation of the solid, e.g. above the solubility limit.

A unique aspect of this method is that it can be used to yield three different useful products. The first is the solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate in equilibrium with its saturated solution. The solid need not be isolated from the saturated solution. Instead, the combination product, a slurry, may be advantageously packaged and transported to a separate location for subsequent reconstitution by simple addition of water to yield an aqueous stabilized, liquid bromine composition whose concentration can be tailored to the amount of reconstitution water used. The second and third products are the solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate and the solid alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate, respectively. These high-activity solids are stable and dissolve rapidly and completely to yield a highly concentrated bromine containing solution.

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by other steps as discussed below depending on whether the desired product is the slurry of the hydrated solid in equilibrium with its saturated solution or one of the two isolated solid products.

a. Utilizing a bromine compound in the oxidation state of -1.

Anhydrous hydrogen bromide gas or aqueous hydrogen bromide may be used. Typically, anhydrous hydrogen bromide gas is emitted from a reactor where bromination of an organic compound to form a brominated flame retardant is taking place. Aqueous hydrogen bromide is a preferred starting reagent and can be used at any concentration up to 70% by weight, but 48% is especially convenient to use as this is the concentration at which the product does not appreciably fume HBr vapors. When aqueous hydrogen bromide is the starting reagent, the process of this invention is conducted under conditions of extreme acidity, preferably at a pH which is greater than about -1 and less than about +1.

b. Introducing to the reaction medium a highly concentrated solution of hydrogen peroxide to effect a full or partial oxidation of the Br moieties into bromine.



Strong solutions of hydrogen peroxide are preferably introduced to anhydrous hydrogen bromide or 48% aqueous hydrogen bromide solution, although this order of addition can be changed without appreciably effecting the reaction. Hydrogen peroxide is commercially available at concentrations up to 90%, although 50% hydrogen peroxide is safer to use and is more commonly available. When an all-aqueous reaction medium is preferred, 50% hydrogen peroxide is added slowly and with stirring to a solution of 48% aqueous hydrogen bromide calculated to have a pH of about -0.78. When a gas-liquid reaction medium is preferred, anhydrous hydrogen bromide gas is bubbled through a solution of 50% hydrogen peroxide. In either case, the amount of 50% hydrogen peroxide used should be sufficient to oxidize between 10% and 100% of the stoichiometric amount, and most preferably between 20% and 80% of the stoichiometric amount of the Br moieties into bromine. The oxidation of anhydrous hydrogen bromide gas or aqueous 48% aqueous hydrogen bromide with 50% hydrogen per-

oxide is an exothermic reaction. Heat removal is effected by conducting the reaction at the refluxing temperature of the reaction mixture using a condenser to facilitate the heat removal process. Alternatively, cooling is effected with a jacketed reactor. The reaction time and temperature are controlled in order to maximize the conversion of Br moieties into bromine and minimize the amount of unreacted hydrogen peroxide remaining in the reaction medium.

c. Mixing a complexing agent to the fully or partially oxidized solution.

On allowing the highly acidic, bromine-laden reaction mixture to cool, a complexing agent is introduced to the same reactor. Preferably the complexing agent is sulfamic acid. The amount of sulfamic acid added depends on the amount of anhydrous hydrogen bromide or aqueous hydrogen bromide originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to Br moiety is advantageous to the stability of the final product with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

In the event that the reaction medium is 100% oxidized by hydrogen peroxide in step (b), steps (d)-(f) are not performed and the method continues with step (g) with subsequent steps depending on whether the desired product is the slurry of the hydrated solid in equilibrium with its saturated solution or one of the two isolated solid products. In the event that the reaction medium is only partially oxidized in step (b), steps (d)-(f) are performed, followed by step (g) and subsequent steps depending on whether the desired product is the slurry of the hydrated solid in equilibrium with its saturated solution or one of the two isolated solid products.

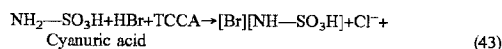
The next step is either (d) or (e).

d. Adding a solid alkaline source to the reaction medium to adjust its pH to between about 0.5 and about 9 and preferably between about 1.0 and about 4.5, followed by introducing sufficient solid organic halogenating agent to oxidize all or substantially all of the remaining bromide ions into bromine.

Any solid alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. A particularly preferred solid alkaline source is NaOH. The solid sodium hydroxide is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F.

Solid organic halogenating agents include any organic compound in which one or more halogen atoms such as Cl, Br, or I is present in the oxidation state of +1 and is covalently bound to a nitrogen or phosphorus atom within the same molecule. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichlorisocyanurate (NaDCC), sodium dichlorisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide.

A particularly preferred source of a solid, organic halogenating agent is trichloroisocyanuric acid (TCCA), which reacts according to the following equation:



Preferably this is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the TCCA reacts, the coarse granules

disappear. The reaction is considered to be complete when no more coarse granules are evident. Although dry, granular TCCA is favored because of its easy handling characteristics, and for providing a visual signal that the reaction is complete, TCCA powdered wetcake may also be employed. The advantage of using TCCA wetcake is that it may be taken directly from the TCCA-producing reactors and so costs associated with drying and granulation of the material are eliminated.

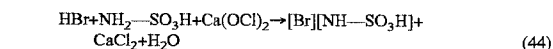
If step (d) is used, step (e) is not used. If step (d) is not used, step (e) is used.

e. Adding a solid alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of bromine compound in the oxidation state of -1 to hydroxide is between about 0.5:1 and about 1:2, preferably between about 1:1, followed by introducing sufficient solid inorganic halogenating agent to oxidize all or substantially all of the remaining bromide ions into bromine.

Any solid alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. A particularly preferred solid alkaline source is NaOH. The solid sodium hydroxide is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F.

Solid inorganic halogenating agents include, but are not limited to, alkali metal and earth alkali metal hypochlorite salts. Suitable examples include lithium hypochlorite, calcium hypochlorite, and magnesium hypochlorite. Due to its low cost and high available chlorine content, calcium hypochlorite is particularly preferred. The higher strength granular forms of the product (containing 65-75% available chlorine) are most preferred.

Under acidic conditions (pH between about -1 and about 5), the oxidation reaction is virtually instantaneous, and proceeds to completion in a short time. The calcium hypochlorite is preferably added rapidly and with good mixing in order to minimize loss of bromine vapors from the reaction medium, but not too quickly such that that phase separation of elemental bromine becomes apparent at the bottom of the reactor. When the addition of the solid calcium hypochlorite is complete, all the sulfamic acid has solubilized to yield an acidic reaction medium. Preferably the calcium hypochlorite is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the calcium hypochlorite reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident.



f. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation.

When the solid organic halogenating agent is TCCA, cyanuric acid is a reaction by-product that is insoluble in the reaction medium (see reaction (43)). Filtration of the cyanuric acid (CA) residue is carried out at pH 1-9, but preferably at about pH 1-6 to maximize CA recovery from solution and minimize the amount of bromine that fumes from the reaction medium. Upon washing the filtercake with water to remove the mother liquors, a highly pure CA wetcake is recovered. This can be recycled to other pro-

cesses to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

If desired, this step can be modified so that the sodium salt of cyanuric acid is recovered from the reaction medium instead of cyanuric acid. This is accomplished by introducing, before performing the solid-liquid separation, sufficient solid NaOH to react with cyanuric acid according to the following equation:

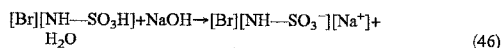


The amount of solid sodium hydroxide solution employed depends on the amount of solid organic halogenating agent used in step (d). When TCCA is the solid organic halogenating agent, sufficient solid NaOH is introduced slowly with mixing and cooling to convert all or substantially all of the cyanuric acid liberated in reaction (43) into its monosodium salt via reaction (45). Monosodium cyanurate is insoluble in the reaction medium at pH < 9. As is true of cyanuric acid, monosodium cyanurate can be separated and recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention. This is accomplished by performing a solid-liquid separation, as described above, which is done when the pH stabilizes at about 9.

When the solid inorganic halogenating agent is calcium hypochlorite, insoluble reaction by-products include calcium carbonate, lime, and quicklime. Filtration of the reaction medium is carried out at pH 1-9, but preferably at about pH 4-8 to reduce the problem of CO<sub>2</sub> gas being liberated from calcium carbonate and also minimize the amount of bromine that fumes from the reaction medium.

g. Adding a solid alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of bromine compound in the oxidation state of -1 to hydroxide is between about 1:2 and about 1:5, preferably between about 1:3 and about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (f).

Any solid alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. A particularly preferred source of alkali metal or earth alkali metal hydroxide is solid NaOH. The sodium hydroxide is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (46).



The amount of NaOH employed depends on the initial charge of bromine compound in the oxidation state of -1. The overall mole ratio of bromine compound in the oxidation state of -1 to NaOH added in steps (d) or (e), if performed, and (g) is in the range of about 1:2 to about 1:5, preferably about 1:3 to about 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its monosodium salt as described in step (f).

h. Removing any further insoluble reaction by-products that develop with a conventional solid-liquid separation technique.

As noted above, any suitable solid-liquid separation technique may be employed. Generally, when TCCA is the halogenating agent, almost 90% of CA reaction by-product

is recovered as a highly pure wetcake in the first solid-liquid separation operation described in step (f). While not wishing to be bound by theory, it is believed that salts of cyanuric acid are precipitated from the reaction mother liquors upon the addition of alkaline sources. When the alkaline source is, for example, solid sodium hydroxide, the mono-, di-, and trisodium salts of cyanuric acid are precipitated. Although insoluble in the reaction mother liquors, the di and trisodium salts display exceptional solubility in ordinary water and are thus useful water treating agents in their own right. However, in comparison to the amount of solids recovered in step (f), the amount of solid that may subsequently develop is relatively low and step (h) may require only a polishing solid-liquid separation, with, for example, a cartridge filter. Moreover, the two solid-liquid separation steps of (f) and (h) may be combined into a single operation performed only at step (f).

i. Chilling, seeding, evaporating, or otherwise promoting crystallization of the bromine-containing salt from its supersaturated solution.

Crystallization of the bromine-containing solid from its supersaturated solution may be achieved by any conventional means. These methods include, but are not limited to, chilling the reaction medium to reduce the solubility of the bromine-containing salt even further to trigger the precipitation process, seeding the reaction medium with bromine-containing salts obtained in an earlier crop so as to provide a surface on which additional crystals are encouraged to nucleate and grow, and evaporating the reaction medium under vacuum to drive off solvent water and promote the crystallization process.

In certain situations, it may be desirable to conclude the method at this point and leave the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate in equilibrium with its saturated solution. This combination product, a slurry, may be advantageously packaged and transported to a separate location for subsequent reconstitution by simple addition of water to yield an aqueous stabilized liquid bromine-containing composition whose concentration can be tailored to the amount of reconstitution water used.

j. Recovering the resultant solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate.

Any suitable solid-liquid separation technique can be employed to separate crystals of the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate from the reaction mother liquors. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. The solid recovered is the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate as a crystalline material.

In order to obtain the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate, the hydrated solid must be dried. Any suitable drying technique may be employed to dry the solid. Suitable examples include, but are not limited to, fluidized bed drying, vacuum oven drying, flash drying, and drying over desiccant, such as molecular sieves. Upon dehydration, the solid that is recovered is the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate.

#### EXAMPLE 16

To a stirred reaction flask containing 48% HBr (69.5 g) was added 50% H<sub>2</sub>O<sub>2</sub> (10.6 g) dropwise so that the reaction flask temperature did not exceed 142° F. After allowing the reaction flask to cool to about 90° F., solid sulfamic acid (48 g) was introduced. The resulting slurry was stirred as solid

sodium hydroxide pellets were charged to the reaction flask. The flask was chilled during this process so that the temperature did not exceed 80° F. A single charge of granular trichloroisocyanuric acid (22.0 g) was introduced to the reaction flask that was stirred for about 20 minutes. Not all the coarse TCCA granules were observed to have reacted during this time, and so deionized water (5 ml) was added to the reactor to assist the process. As the reaction proceeded, a fine powdery precipitate developed which was removed by vacuum filtration. Then additional solid NaOH pellets (17 g) were introduced also with cooling and at a rate such that the temperature did not exceed 80° F. Any additional precipitate that developed was immediately removed by vacuum filtration. Iodometric titration of the resulting golden yellow solution was used to determine its Br<sub>2</sub> content of 27.2% (or 12.1% as Cl<sub>2</sub>). Within a few minutes, this highly concentrated bromine solution started to turn turbid as crystals began to form. The crystallizing solution was chilled in an ice bath to expedite the development of the crystals. A large crop of yellow crystalline material was separated by vacuum filtration, and the mother liquors were retitrated iodometrically. The new bromine content was found to be 24.3% (10.8% as Cl<sub>2</sub>), indicating that the solution had lost soluble oxidant as the solids crystallized. The yellow crystalline material displayed exceptionally high solubility in water. The dissolution process was rapid and complete. There were no insoluble residues. Iodometric titration of resulting solutions was used to calculate that the crystalline solid contained 29.9% Br<sub>2</sub> (13.1% as Cl<sub>2</sub>).

#### The Fifth Embodiment

The fifth embodiment is a method of producing heretofore unknown, highly water soluble, bromine-containing solid compositions of matter, namely, the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate and the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate. The method uses alkali metal or earth alkali metal bromide ion solutions under reaction conditions designed to promote the formation of the solid, e.g. above the solubility limit.

A unique aspect of this method is that it can be used to yield three different useful products. The first is the solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate in equilibrium with its saturated solution. The solid need not be isolated from the saturated solution. Instead, the combination product, a slurry, may be advantageously packaged and transported to a separate location for subsequent reconstitution by simple addition of water to yield an aqueous stabilized, liquid bromine composition whose concentration can be tailored to the amount of reconstitution water used. The second and third products are the solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate and the solid alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate, respectively. These high-activity solids are stable and dissolve rapidly and completely to yield a highly concentrated bromine containing solution.

The method preferably includes the following steps. Steps (a), (b), and (c) may be performed in any order, or simultaneously, followed by other steps depending on whether the desired product is the slurry of hydrated solid in equilibrium with its saturated solution or one of the two isolated solid products.

a. Utilizing an alkali metal or earth alkali metal solution of bromide ions.

Sources of alkali metal or earth alkali metal solutions of bromide ion include, but are not limited to, lithium bromide, sodium bromide, potassium bromide, calcium bromide, and magnesium bromide. A preferred source of bromide ion solution is sodium bromide solution, commonly available as a 40–46% aqueous solution, or it may be made into such a solution by dissolving solid sodium bromide salt in water.

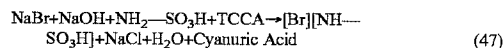
b. Mixing a complexing agent to the bromide ion solution.

Preferably, the complexing agent is sulfamic acid. The amount of sulfamic acid added depends on the amount of bromide ion originally present. A mole ratio of about 0.75:1 to about 1.5:1 sulfamic acid to sodium is advantageous to the stability of the final product, with about 0.95:1 to about 1.2:1 being the most preferred mole ratio range.

c. Adding an alkaline source to the reaction medium to adjust its pH to between about 0.5 and about 9 and preferably between about 1.0 and about 4.5, followed by introducing sufficient solid, organic halogenating agent to oxidize all or substantially all of the bromide ions into bromine.

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted with water and used in the process of this invention. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F.

Solid organic halogenating agents include any organic compound in which one or more halogen atoms such as Cl, Br, or I is present in the oxidation state of +1 and is covalently bound to a nitrogen or phosphorus atom within the same molecule. Suitable examples include, but are not limited to, trichloroisocyanuric acid (TCCA), sodium dichloroisocyanurate (NaDCC), sodium dichloroisocyanurate dihydrate (NaDCC.2H<sub>2</sub>O), trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide. A particularly preferred source of a solid, organic halogenating agent is trichloroisocyanuric acid (TCCA). Preferably this is used in the form of a coarse granular grade of material for ease of introduction to the stirred, cooled reactor. As the TCCA reacts, the coarse granules disappear. The reaction is considered to be complete when no more coarse granules are evident. Although dry, granular TCCA is favored because of its easy handling characteristics and for providing a visual signal that the reaction is complete, TCCA powdered wetcake may also be employed. The advantage of using TCCA wetcake is that it may be taken directly from the TCCA-producing reactors, and so costs associated with drying and granulation of the material are eliminated.



d. Removing any insoluble reaction by-products with a conventional solid-liquid separation technique.

Any suitable solid-liquid separation technique can be employed. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and

vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation.

When the solid organic halogenating agent is TCCA, cyanuric acid is a reaction by-product that is insoluble in the reaction medium. Filtration of the cyanuric acid (CA) residue is carried out at pH 1-9, but preferably at about pH 1-6 to maximize CA recovery from solution and minimize the amount of bromine that fumes from the reaction medium (see reaction (44)). Upon washing the filtercake with water to remove the mother liquors, a highly pure CA wetcake is recovered. This can be recycled to other processes to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention.

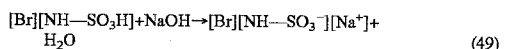
If desired, this step can be modified so that the sodium salt of cyanuric acid is recovered from the reaction medium instead of cyanuric acid. This is accomplished by introducing, before performing the solid-liquid separation, sufficient 50% NaOH solution to react with cyanuric acid according to the following equation:



The amount of 50% sodium hydroxide solution employed depends on the amount of solid organic halogenating agent used in step (c). When TCCA is the solid organic halogenating agent, sufficient 50% NaOH solution is introduced slowly with mixing and cooling to convert all or substantially all of the cyanuric acid liberated in reaction (47) into its monosodium salt via reaction (48). Monosodium cyanurate is insoluble in the reaction medium at pH<9. As is true of cyanuric acid, monosodium cyanurate can be separated and recycled to other processes in order to make additional quantities of TCCA, NaDCC, or NaDCC.2H<sub>2</sub>O that can be used in the method of the current invention. This is accomplished by performing a solid-liquid separation, as described above, which is done when the pH stabilizes at about 9.

e. Adding an alkaline source to the reaction mother liquors such that if the alkaline source is a hydroxide salt, the overall mole ratio of aqueous alkali metal or earth alkali metal bromide to hydroxide is between about 1:2 and about 1:5, preferably between about 1:3 and 1:4. This does not include any hydroxide salt that may be used to convert cyanuric acid into its alkali metal or earth alkali metal salt as described in step (d).

Any alkaline source may be employed. Examples include, but are not limited to, alkali metal or earth alkali metal carbonates, bicarbonates, oxides, and hydroxides. When solutions are preferred, sodium hydroxide or potassium hydroxide solutions are convenient to use, alone or in combination with each other. A particularly preferred alkaline source is 50% NaOH solution. To prevent storage problems in cold climates, 50% NaOH solution may be diluted to 25% and used. The sodium hydroxide solution is introduced to the reaction medium slowly, and with stirring and cooling such that the temperature preferably does not exceed 80° F. The purpose is to deprotonate the bromo derivative of sulfamic acid to form the bromo derivative of sodium sulfamate according to reaction (49).



The amount of 50% NaOH solution employed depends on the initial charge of aqueous alkali metal or earth alkali metal bromide. The overall mole ratio of aqueous alkali metal or earth alkali metal bromide to NaOH added in steps (c) and (e) is in the range of about 1:2 to about 1:5, preferably about 1:3 to about 1:4. This does not include any

hydroxide salt that may be used to convert cyanuric acid into its monosodium salt as described in step (d).

f. Removing any further insoluble reaction by-products that develop with a conventional solid-liquid separation technique.

As noted above, any suitable solid-liquid separation technique may be employed. Generally, when TCCA is the halogenating agent, almost 90% of CA reaction by-product is recovered as a highly pure wetcake in the first solid-liquid separation operation described in step (d). While not wishing to be bound by theory, it is believed that salts of cyanuric acid are precipitated from the reaction mother liquors upon the addition of alkaline sources. When the alkaline source is, for example, 50% sodium hydroxide solution, the mono-, di-, and trisodium salts of cyanuric acid are precipitated. Although insoluble in the reaction mother liquors, the di and trisodium salts display exceptional solubility in ordinary water and are thus useful water treating agents in their own right. However, in comparison to the amount of solids recovered in step (d), the amount of solid that may subsequently develop is relatively low and step (f) may require only a polishing solid-liquid separation, with, for example, a cartridge filter. Moreover, the two solid-liquid separation steps of (d) and (f) may be combined into a single operation performed only at step (d).

g. Chilling, seeding, evaporating, or otherwise promoting crystallization of the bromine-containing salt from its supersaturated solution.

Crystallization of the bromine-containing solid from its supersaturated solution may be achieved by any conventional means. These methods include, but are not limited to, chilling the reaction medium to reduce the solubility of the bromine-containing salt even further to trigger the precipitation process, seeding the reaction medium with bromine-containing salts obtained in an earlier crop so as to provide a surface on which additional crystals are encouraged to nucleate and grow, and evaporating the reaction medium under vacuum to drive off solvent water and promote the crystallization process.

In certain situations, it may be desirable to conclude the method at this point and leave the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate in equilibrium with its saturated solution. This combination product, a slurry, may be advantageously packaged and transported to a separate location for subsequent reconstitution by simple addition of water to yield an aqueous stabilized liquid bromine-containing composition whose concentration can be tailored to the amount of reconstitution water used.

h. Recovering the resultant solid alkali metal or earth alkali metal salt of hydrated N-bromosulfamate.

Any suitable solid-liquid separation technique can be employed to separate crystals of alkali metal or earth alkali metal salt of hydrated N-bromosulfamate from the reaction mother liquors. Suitable examples include, but are not limited to, centrifugation, clarification, gravity sedimentation, and vacuum filtration. Filtration is a particularly preferred technique for effecting solid-liquid separation. The solid recovered is the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate as a crystalline material.

In order to obtain the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate, the hydrated salt must be dried. Any suitable drying technique can be employed to dry the solid. Suitable examples include, but are not limited to, fluidized bed drying, vacuum oven drying, flash drying, and drying over dessicant, such as molecular sieves. The solid that is recovered is the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate.

## EXAMPLE 17

To a stirred reaction flask containing 40% sodium bromide solution was added solid sulfamic acid (82.3 g). The resultant slurry was stirred as 50% sodium hydroxide (60.2 g) was introduced. The flask was chilled during this process so that the temperature did not exceed 80° F. A single charge of trichlorocyanuric acid (55 g) was then introduced to the stirred reaction flask. However, the reaction medium became very viscous, and this hampered the mixing efficiency, so deionized water (35.8 g) was added to thin the mixture. The fine powdery precipitate that developed was removed by vacuum filtration. Then, 50% NaOH solution (10 g) was added also with cooling and at such a rate that the temperature did not exceed 80° F. Any additional solid that developed during this addition process was immediately removed by vacuum filtration. Iodometric titration of the resulting golden yellow solution was used to determine its bromine content of 22.7% as Br<sub>2</sub> (10.1% as Cl<sub>2</sub>) which corresponded to 100% yield. On standing for two days in a cool environment, a single, large crystalline mass weighing 33 g had developed. The mother liquors were determined to have a bromine content of 20.9% as Br<sub>2</sub> (9.3% as Cl<sub>2</sub>) by iodometric titration. The crystalline mass was observed to comprise mainly regular rhombohedral crystals, possessing a yellow glass-like appearance. A section of the crystalline mass was dissolved in water. It dissolved rapidly and completely. Iodometric titration of the solution was used to calculate that the crystalline solid contained 47.2% as Br<sub>2</sub> (21% as Cl<sub>2</sub>).

## The Sixth Embodiment

The sixth embodiment of this invention is a stable, liquid composition of matter that contains 60–80% more available bromine than the two products that are currently available. One product, described in U.S. Pat. Nos. 5,683,654, 5,795, 487, 5,942,126, and 6,136,205, is prepared from a process using sodium hypochlorite solution. It is reported to contain 14% as Br<sub>2</sub> (6.3% as Cl<sub>2</sub>). The other product, described in U.S. Pat. Nos. 6,068,861, 6,495,169, and 6,322,822, is prepared from a process using bromine chloride. It is reported to contain 15.5% as Br<sub>2</sub> (6.9% as Cl<sub>2</sub>). Further, U.S. Pat. Nos. 6,299,909, 6,306,441, and 6,348, 219 disclose an upper ceiling of 18% as Br<sub>2</sub> (8% as Cl<sub>2</sub>) as the highest strength concentrate that could be made by the bromine chloride process. The composition of the sixth embodiment is low in dissolved halide ion salts, permitting it to contain greater than about 18% as Br<sub>2</sub> (8% as Cl<sub>2</sub>) and still maintain excellent physical and chemical stability. This composition may be prepared using the methods of the first, second, and third embodiments of the invention.

The bromine-containing aqueous composition has the following attributes and advantages:

- (1) It has an active ingredient content of at least about 18% as Br<sub>2</sub> (8% as Cl<sub>2</sub>);
- (2) It is prepared to contain between zero and about 1 mole of dissolved halide ion salts per mole of active halogen (expressed as Br<sub>2</sub> or Cl<sub>2</sub>);
- (3) It has an active ingredient content in which most of the halogen is present as bromine;
- (4) It has chemical stability with an active ingredient half-life of at least about 58 days at about 125° F;
- (5) It has physical stability as being devoid of solid precipitates, nor strongly prone to the development of solid precipitates on storage;
- (6) It has physical stability to at least about three cycles of freezing and thawing; and
- (7) It has an undetectable level of bromate ion.

None of the previously reported solutions exhibits all of these attributes. None of the previously reported commercially available solutions has an active ingredient content as high as 18% as Br<sub>2</sub> (8% as Cl<sub>2</sub>). All of the commercially available solutions, when prepared, have at least 1–2 moles of dissolved halide ion salts per mole of active halogen (expressed as Br<sub>2</sub> or Cl<sub>2</sub>).

## EXAMPLE 18

The chemical and physical stability of the aqueous bromine solutions were assessed at elevated temperatures. Samples were poured into capped plastic containers and placed in an oven held between 120–130° F. The chemical stability was determined by measuring the amount of active ingredient remaining in the formulation as a function of time. The physical stability was established by visual observation of whether any solids precipitated from solution over the same period and were evident on the side or bottom of the container, or floating on the surface of the solution. The data in Table V shows the chemical and physical stability of a sample prepared according to Example 5 described earlier.

TABLE V

Day	Chemical Stability of Active Ingredient		Physical Stability
	Wt. % Cl <sub>2</sub>	% Remaining	Precipitation?
0	10.83	100	None
26	8.61	79.5	None
30	8.41	77.6	None
37	8.25	76.2	None
44	7.67	70.8	None
54	7.33	67.6	Slight
58	7.01	64.7	Slight

## EXAMPLE 19

The freeze-thaw cyclability of the aqueous bromine concentrate prepared in Example 5 was assessed by freezing a sample in the freezer compartment of a refrigerator followed by thawing. The temperature of the frozen composition was recorded immediately upon removing it from the freezer (the chill temperature). As the sample thawed, the temperature at which the last crystal to disappear was measured. Table VI summarizes the observations.

TABLE VI

Cycle Number	Chill Temperature/° F.	Last Crystal to Disappear/° F.
1	13.4	49
2	23.8	49.6
3	2.1	130

## EXAMPLE 20

The biocidal performance of the liquid composition of the present invention was compared to a solution of sodium bromide activated using an equimolar amount of sodium hypochlorite bleach, and a solution prepared from 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH). Sterile phosphate buffer samples (pH 8.5) were inoculated with *Pseudomonas aeruginosa* to give a concentration of

45

approximately  $5 \times 10^6$  bacteria/ml and then challenged with the test systems at a nominal concentration of 0.2 ppm total halogen (as  $\text{Cl}_2$ ).

After a contact time of 10 minutes at  $35^\circ \text{C}$ ., an aliquot of sodium thiosulfate was added to each sample to neutralize the halogen. The level of viable bacteria in each sample was determined by plate counting. Plates were incubated at  $35^\circ \text{C}$ . for 48 hours. The results expressed as log reduction in viable bacteria/ml are summarized in Table VII below.

TABLE VII

Test Sample	Nominal dose of total halogen/ ppm as $\text{Cl}_2$	Measured dose of total halogen/ ppm as $\text{Cl}_2$	Viable bacteria/ ml after 10 minutes	Log Reduction
Control	—	—	$5.3 \times 10^6$	—
Present invention	0.2	0.19	$2.5 \times 10^3$	3.3
NaBr/NaOCl	0.2	0.14	$2.1 \times 10^2$	4.4
BCDMH	0.2	0.17	$2.5 \times 10^3$	3.3

Thus, the biocidal performance of the liquid composition of the present invention was comparable to that of other bromine-based biocides.

## EXAMPLE 21

Anion chromatography was used to measure the amount of bromate ion present in the solutions of the present invention. A sample that had been prepared 32 days earlier was analyzed using the technique. Bromate was measured at less than 50 ppm, which is below the detection limit of the method. Thus, bromate is not formed in the reaction process, nor is it formed as the sample ages.

## The Seventh Embodiment

The seventh embodiment of this invention is a stable, liquid mixed halogen composition that contains both bromine and chlorine. Typically, the composition is low in dissolved halide ion salts, permitting it to contain a total halogen level greater than 21% when expressed as  $\text{Br}_2$  (9.4% when expressed as  $\text{Cl}_2$ ). The composition may, however, contain a total halogen level as low as 2.25% when expressed as  $\text{Br}_2$  (1% when expressed as  $\text{Cl}_2$ ). The ratio of bromine to chlorine in the composition can vary. A useful mixed halogen composition may contain 50 mole % bromine: 50 mole % chlorine and up to 90 mole % bromine: 10 mole % chlorine. The mixed halogen composition may be prepared using the methods of the second and third embodiments of the invention.

The mixed halogen composition has the following attributes and advantages:

- (1) It has a total halogen content of at least 2.25% when expressed as  $\text{Br}_2$  (1% when expressed as  $\text{Cl}_2$ );
- (2) It has between zero and less than 1 mole of dissolved halide ion salts per mole of active halogen (expressed as  $\text{Br}_2$  or  $\text{Cl}_2$ );
- (3) It has an active ingredient content in which the halogen is present as both bromine and chlorine;
- (4) A 50 mole % bromine: 50 mole % chlorine mixed halogen composition with a total halogen content of 21% when expressed as  $\text{Br}_2$  (9.4% when expressed as  $\text{Cl}_2$ ) has a chemical stability such that more than 90% of the active ingredient remains after 34 days storage at  $120^\circ \text{F}$ ;

46

- (5) It has physical stability as being devoid of solid precipitates, nor strongly prone to the development of solid precipitates; and
- (6) It has an undetectable level of bromate ion.

## EXAMPLE 22

The chemical stability of the mixed halogen solution prepared in Example 15 was assessed at ambient and elevated temperatures. The sample was poured into a capped plastic container and placed in an oven held at  $120^\circ \text{F}$ . The amount of active ingredient remaining in the composition was monitored as a function of time. The physical stability was established by visual observation of whether any solids precipitated from solution over the same period and were evident on the side or bottom of the container, or floating on the surface of the solution. The data in Table VIII shows the results. It can be seen that even after one month at  $120^\circ \text{F}$ ., less than 10% of the halogen has been depleted and there was no evidence of solids formation in either the ambient temperature or  $120^\circ \text{F}$ . samples.

TABLE VIII

Day	Ambient Temperature			$120^\circ \text{F}$ .		
	Solids Formed?	Wt. % $\text{Cl}_2$	% Remaining	Wt. % $\text{Cl}_2$	% Remaining	Solids Formed?
0	No	9.39	100	9.39	100	No
12	No	9.21	98.1	8.8	93.7	No
19	No	9.07	96.6	8.65	92.1	No
34	No	9.15	97.4	8.56	91.1	No

## The Eighth Embodiment

The eighth embodiment of this invention is two bromine-containing solid compositions of matter: (1) the alkali metal or earth alkali metal salt of hydrated N-bromosulfamate; and (2) the alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate. These compositions may be prepared using the methods of the fourth and fifth embodiments of the invention.

The solid compositions have the following attributes and advantages:

- (1) They dissolve quickly and completely in water to yield high-strength bromine-containing solutions;
- (2) They can be applied directly to water in order to rapidly furnish that water with active bromine;
- (3) The alkali metal or earth alkali metal salt of hydrated N-bromosulfamate is completely stable in equilibrium with its saturated solution such that the slurry may be advantageously packaged and transported to a separate location for subsequent reconstitution by the simple addition of water to yield an aqueous stabilized liquid bromine-containing composition whose concentration can be tailored to the amount of reconstitution water used; and
- (4) The alkali metal or earth alkali metal salt of anhydrous N-bromosulfamate is extremely stable if kept dry and in vacuo (see Example 24). Therefore, the product may be advantageously packaged and transported to a separate location for subsequent reconstitution by the simple addition of water to yield an aqueous stabilized liquid bromine-containing composition whose concentration can be tailored to the amount of reconstitution water used.



The crystals recovered from solution in Example 17 were manually dried of the reaction mother liquors with a paper towel. The crystals were glass-like, yellow, regular rhombohedra. Iodometric titration to determine the oxidizing activity of the crystals meant dissolving some of the solid in water. They dissolved quickly and completely. The result of the titration revealed that the solid contained 23.6% active bromine (as Br).

A further portion of the towel-dried crystals was dissolved in water for analysis by atomic absorption spectroscopy. The data indicated that it contained 9.35% sodium ion.

A further portion of the towel-dried crystals recovered from Example 17 was weighed out and placed overnight in an oven set to 130° F. The yellow, glass-like, regular rhombohedral crystals had turned to a dull, yellow amorphous powder in the oven. Upon reweighing, a loss of 32% of the original weight was determined. Because the loss in weight was associated with a loss in crystallinity, most of the weight loss was attributed to the removal of water of crystallization molecules.

X-ray fluorescence spectroscopy on the crystals confirmed the presence of sodium, sulfur, and bromine atoms. This information, together with the bromine, sodium, and water content, indicated that the solid was the sodium salt of hydrated N-bromosulfamate designated by the formula  $[\text{Na}^+][\text{Br}-\text{NH}-\text{SO}_3^-] \cdot n\text{H}_2\text{O}$ .

Another large portion of the crystalline mass was dried with a paper towel and placed in a ceramic crucible that was heated on a hot plate. At about 221° F., the water of crystallization molecules were observed to boil from the product, which then decomposed and evolved dark red bromine vapors. A white residue was left behind, which was found to be extremely soluble in water.

X-ray diffraction spectroscopy on the crystals yielded a characteristic diffraction pattern. The responses due to likely contaminants associated with the solid (NaCl, NaOH,  $\text{Na}_2\text{SO}_4$ ) were subtracted from the spectrum. The diffraction angle data (2 Theta) and the relative intensities of the responses are shown in Table IX.

TABLE IX

2 Theta/degrees	Intensity
12.14	3189
14.52	1203
14.78	1181
16.00	588
16.36	524
16.54	743
16.76	1983
20.70	1988
24.34	3294
26.96	1170
27.68	1819
28.26	1524
28.52	3294
29.66	2912
30.28	948
36.76	1019
39.16	1031
39.26	654
41.94	548
43.96	633
45.52	841
45.82	315
46.00	531
46.18	900
48.14	545

TABLE IX-continued

2 Theta/degrees	Intensity
50.78	454
52.50	295
52.90	344

## EXAMPLE 24

A further portion of the towel dried crystals from Example 17 was dehydrated by placing in a vacuum dessicator containing molecular sieves. After 15 days, a loss of 31% of the original weight was determined. Although the crystals lost their glass-like appearance, the rhombohedral shape was retained. The loss in weight was correlated with an increase in active ingredient content to 33.6% as Br. Hence, this solid is the sodium salt of anhydrous N-bromosulfamate designated by the formula  $[\text{Na}^+][\text{Br}-\text{NH}-\text{SO}_3^-]$ .

The sodium salt of anhydrous N-bromosulfamate was placed back in the vacuum dessicator. After three months of storage at room temperature, it was re-analyzed and determined not to have lost any activity.

The invention has been described above with reference to the preferred embodiments. Those skilled in the art may envision other embodiments and variations of the invention which fall within the scope of the claims.

We claim:

1. A method of preparing a liquid, bromine-containing solution, comprising:

- combining a complexing agent, hydrogen peroxide, and anhydrous hydrogen bromide gas; and
- adding an alkaline source.

2. The method of claim 1, wherein said complexing agent is sulfamic acid, and further, wherein the mole ratio of said sulfamic acid to said anhydrous hydrogen bromide is between about 0.75:1 and about 1.5:1.

3. The method of claim 2, wherein said alkaline source is selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

4. The method of claim 3, wherein said alkaline source is an alkali metal hydroxide, and further, wherein said alkali metal hydroxide is 50% sodium hydroxide solution.

5. A method of preparing a liquid, bromine-containing solution, comprising:

- combining a source of bromide ions, hydrogen peroxide, and a complexing agent; and
- adding an alkaline source.

6. The method of claim 5, wherein said source of bromide ions is aqueous hydrogen bromide and said complexing agent is sulfamic acid, and further, wherein the mole ratio of said sulfamic acid to said aqueous hydrogen bromide is between about 0.75:1 and about 1.5:1.

7. The method of claim 5, further comprising after step a but before step b, adding a solid halogenating agent and another alkaline source, and then conducting a solid-liquid separation.

8. The method of claim 7, wherein said solid halogenating agent is an organic halogenating agent.

9. The method of claim 8, wherein said organic halogenating agent is selected from the group consisting of trichloroisocyanuric acid, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, potassium dichloroisocyanurate, dichloroisocyanuric acid, trichloromelamine,



N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide.

10. The method of claim 9, wherein said organic halogenating agent is trichloroisocyanuric acid.

11. The method of claim 7, wherein said solid halogenating agent is an inorganic halogenating agent.

12. The method of claim 11, wherein said inorganic halogenating agent is selected from the group consisting of calcium hypochlorite, lithium hypochlorite, and magnesium hypochlorite.

13. The method of claim 12, wherein said inorganic halogenating agent is calcium hypochlorite.

14. The method of claim 7, wherein said alkaline sources are selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

15. The method of claim 14, wherein said alkaline sources are alkali metal hydroxides, and further, wherein said alkali metal hydroxides are 50% sodium hydroxide solution.

16. A method of preparing a liquid bromine- and chlorine-containing solution, comprising:

- a. combining a source of bromine ions, hydrogen peroxide and a complexing agent;
- b. adding a first alkaline source and a solid chlorinating agent;
- c. conducting a solid-liquid separation; and
- d. adding a second alkaline source.

17. The method of claim 16, wherein the molar equivalent of the combination of said hydrogen peroxide and said solid chlorinating agent is in excess of the molar equivalent of said bromide ions.

18. The method of claim 16, wherein said source of bromide ions is aqueous hydrogen bromide and said complexing agent is sulfamic acid, and further, wherein the mole ratio of said sulfamic acid to total halogen is between about 0.75:1 and about 1.5:1.

19. The method of claim 16, wherein said solid chlorinating agent is an organic chlorinating agent.

20. The method of claim 19, wherein said organic chlorinating agent is selected from the group consisting of trichloroisocyanuric acid, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, potassium dichloroisocyanurate, dichloroisocyanuric acid, trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin.

21. The method of claim 20, wherein said organic chlorinating agent is trichloroisocyanuric acid.

22. The method of claim 16, wherein said solid chlorinating agent is an inorganic chlorinating agent.

23. The method of claim 22, wherein said inorganic chlorinating agent is selected from the group consisting of calcium hypochlorite, lithium hypochlorite, and magnesium hypochlorite.

24. The method of claim 23, wherein said inorganic chlorinating agent is calcium hypochlorite.

25. The method of claim 16, wherein said first and said second alkaline sources are selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

26. The method of claim 25, wherein said first and said second alkaline sources are alkali metal hydroxides, and further, wherein said alkali metal hydroxides are 50% sodium hydroxide solution.

27. A method of preparing a liquid, bromine-containing solution, comprising:

- a. combining a source of bromide ions, a complexing agent, and a solid halogenating agent;
- b. conducting a solid-liquid separation; and
- c. adding an alkaline source.

28. The method of claim 27, wherein said source of bromide ions is sodium bromide solution and said complexing agent is sulfamic acid, and further, wherein the mole ratio of said sulfamic acid to said sodium bromide solution is between about 0.75:1 and about 1.5:1.

29. The method of claim 27, wherein said solid halogenating agent is an organic halogenating agent, and further comprising before step b, adding another alkaline source.

30. The method of claim 29, wherein said organic halogenating agent is selected from the group consisting of trichloroisocyanuric acid, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, potassium dichloroisocyanurate, dichloroisocyanuric acid, trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and N-bromosuccinimide.

31. The method of claim 30, wherein said organic halogenating agent is trichloroisocyanuric acid.

32. The method of claim 29, wherein said alkaline sources are selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

33. The method of claim 32, wherein said alkaline sources are alkali metal hydroxides, and further, wherein said alkali metal hydroxides are 50% sodium hydroxide solution.

34. The method of claim 27, wherein said solid halogenating agent is an inorganic halogenating agent.

35. The method of claim 34, wherein said inorganic halogenating agent is selected from the group consisting of calcium hypochlorite, lithium hypochlorite, and magnesium hypochlorite.

36. The method of claim 35, wherein said inorganic halogenating agent is calcium hypochlorite.

37. The method of claim 34, wherein said alkaline source is selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

38. The method of claim 37, wherein said alkaline source is an alkali metal hydroxide, and further, wherein said alkali metal hydroxide is 50% sodium hydroxide solution.

39. A method of preparing a liquid bromine- and chlorine-containing solution, comprising:

- a. combining a source of bromide ions, a complexing agent, and a solid chlorinating agent;
- b. conducting a solid-liquid separation; and
- c. adding an alkaline source.

40. The method of claim 39, wherein said source of bromine ions is sodium bromide solution and said complexing agent is sulfamic acid, and further, wherein the mole ratio of said sulfamic acid to said sodium bromide solution is between about 0.75:1 and about 1:5.1.

51

41. The method of claim 39, wherein a molar excess of said solid chlorinating agent to said bromide ions is employed.

42. The method of claim 41, wherein said solid chlorinating agent is an organic chlorinating agent, and further comprising before step b, adding another alkaline source.

43. The method of claim 42, wherein said organic chlorinating agent is selected from the group consisting of trichloroisocyanuric acid, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, potassium dichloroisocyanurate, dichloroisocyanuric acid, trichloromelamine, N-chloro-p-toluenesulfonamide, N-chloromethanesulfonamide, N-chlorosuccinimide, N,N'-1,3-bromochloro-5,5-dimethylhydantoin, N,N'-1,3-bromochloro-5-ethyl-5-methylhydantoin, and 1,3-dichloro-5,5-dimethylhydantoin.

44. The method of claim 43, wherein said organic chlorinating agent is trichloroisocyanuric acid.

45. The method of claim 42, wherein said alkaline sources are selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

46. The method of claim 45, wherein said alkaline sources are alkali metal hydroxides, and further, wherein said alkali metal hydroxides are 50% sodium hydroxide solution.

47. The method of claim 41, wherein said solid chlorinating agent is an inorganic chlorinating agent.

48. The method of claim 47, wherein said inorganic chlorinating agent is selected from the group consisting of calcium hypochlorite, lithium hypochlorite, and magnesium hypochlorite.

49. The method of claim 48, wherein said inorganic chlorinating agent is calcium hypochlorite.

50. The method of claim 47, wherein said alkaline source is selected from the group consisting of alkali metal carbonate, earth alkali metal carbonate, alkali metal bicarbonate, earth alkali metal bicarbonate, alkali metal oxide, earth alkali metal oxide, alkali metal hydroxide, and earth alkali metal hydroxide.

51. The method of claim 50, wherein said alkaline source is an alkali metal hydroxide, and further, wherein said alkali metal hydroxide is 50% sodium hydroxide solution.

52. A method of preparing a bromine-containing solid, comprising:

- a. combining a bromine compound in the oxidation state of -1, hydrogen peroxide, and a complexing agent;
- b. adding an alkaline source; and
- c. promoting crystallization of a bromine-containing solid.

53. The method of claim 52, further comprising after step a but before step b, adding a solid halogenating agent and another alkaline source, and then conducting a solid-liquid separation.

54. The method of claim 53, wherein said solid halogenating agent is an organic halogenating agent.

55. The method of claim 53, wherein said solid halogenating agent is an inorganic halogenating agent.

56. The method of claim 52, further comprising after step c, recovering said bromine-containing solid.

57. The method of claim 56, wherein said bromine-containing solid is selected from the group consisting of the alkali metal salt of hydrated N-bromosulfamate and the earth alkali metal salt of hydrated N-bromosulfamate.

58. The method of claim 56, further comprising after recovering said bromine-containing solid, dehydrating said solid.

52

59. The method of claim 58, wherein said dehydrated bromine-containing solid is selected from the group consisting of the alkali metal salt of anhydrous N-bromosulfamate and the earth alkali metal salt of anhydrous N-bromosulfamate.

60. A method of preparing a bromine-containing solid in equilibrium with its saturated solution, comprising:

- a. combining a bromine compound in the oxidation state of -1, hydrogen peroxide, and a complexing agent;
- b. adding an alkaline source;
- c. promoting crystallization of a bromine-containing solid; and
- d. recovering a slurry of said bromine-containing solid in equilibrium with its saturated solution.

61. The method of claim 60, further comprising after step a but before step b, adding a solid halogenating agent and another alkaline source, and then conducting a solid-liquid separation.

62. The method of claim 61, wherein said solid halogenating agent is an organic halogenating agent.

63. The method of claim 61, wherein said solid halogenating agent is an inorganic halogenating agent.

64. The method of claim 60, wherein said bromine-containing solid is selected from the group consisting of the alkali metal salt of hydrated N-bromosulfamate and the earth alkali metal salt of hydrated N-bromosulfamate.

65. A method of preparing a bromine-containing solid, comprising:

- a. combining a source of bromide ions, a complexing agent, a first alkaline source, and a solid, organic halogenating agent;
- b. conducting a solid-liquid separation;
- c. adding a second alkaline source; and
- d. promoting crystallization of a bromine-containing solid.

66. The method of claim 65, further comprising after step d, recovering said bromine-containing solid.

67. The method of claim 66, wherein said bromine-containing solid is selected from the group consisting of the alkali metal salt of hydrated N-bromosulfamate and the earth alkali metal salt of hydrated N-bromosulfamate.

68. The method of claim 66, further comprising after recovering said bromine-containing solid, dehydrating said bromine-containing solid.

69. The method of claim 68, wherein said dehydrated bromine-containing solid is selected from the group consisting of the alkali metal salt of anhydrous N-bromosulfamate and the earth alkali metal salt of anhydrous N-bromosulfamate.

70. A method of preparing a bromine-containing solid in equilibrium with its saturated solution, comprising:

- a. combining the source of bromide ions, a complexing agent, a first alkaline source, and a solid, organic halogenating agent;
- b. conducting a solid-liquid separation;
- c. adding a second alkaline source;
- d. promoting crystallization of a bromine-containing solid; and
- e. recovering a slurry of said bromine-containing solid in equilibrium with its saturated solution.

71. The method of claim 70, wherein said bromine-containing solid is selected from the group consisting of the alkali metal salt of hydrated N-bromosulfamate and the earth alkali metal salt of hydrated N-bromosulfamate.

\* \* \* \* \*

# APPENDIX

## J



US005565109A

**United States Patent** [19]**Sweeny**[11] **Patent Number:** **5,565,109**[45] **Date of Patent:** **Oct. 15, 1996**[54] **HYDANTOIN-ENHANCED HALOGEN  
EFFICACY IN PULP AND PAPER  
APPLICATIONS**

4,427,692	1/1984	Girard	424/272
4,537,697	8/1985	Girard	252/90
4,698,165	10/1987	Theyson	210/755
4,925,866	5/1990	Smith	514/389

[75] **Inventor:** **Philip G. Sweeny**, Hackettstown, N.J.**Primary Examiner**—Peter A. Hruskoci[73] **Assignee:** **Lonza Inc.**, Fair Lawn, N.J.**Attorney, Agent, or Firm**—Darby & Darby, P.C.[21] **Appl. No.:** **323,459**

[57]

**ABSTRACT**[22] **Filed:** **Oct. 14, 1994**[51] **Int. Cl.<sup>6</sup>** ..... **C02F 1/50**[52] **U.S. Cl.** ..... **210/755; 210/754; 210/764;**  
210/756; 162/161[58] **Field of Search** ..... 162/161; 210/754,  
210/755, 756, 764[56] **References Cited****U.S. PATENT DOCUMENTS**

3,328,294	6/1967	Self et al.	210/62
3,749,672	7/1973	Golton et al.	252/95
4,297,224	10/1981	Macchiarolo et al.	210/755

Free halogen sources (e.g., sodium hypochlorite and chlorine) added as slimicides in high organic component process streams such as pulp and paper processing are rendered more efficacious by the addition of selected N-hydrogen compounds (namely, 5,5-dimethylhydantoin, 5-ethyl-5-methylhydantoin, cyanuric acid, succinimide, urea, 4,4-dimethyl-2-oxazolidinone, and glycouril) to the process stream. The latter compounds may be added to the process stream before or after the slimicide is added or combined with the slimicide and added directly thereto. The direct use of halogenated hydantoins has also been found to provide improved efficacy relative to free halogen sources. In addition, absorbable organic halogen by-products are reduced.

**13 Claims, No Drawings**

1

# HYDANTOIN-ENHANCED HALOGEN EFFICACY IN PULP AND PAPER APPLICATIONS

## BACKGROUND OF THE INVENTION

Sodium hypochlorite and chlorine gas are commonly used as circulating water slimicides. Upon reaction with organic system components, these materials can produce adsorbable organic halogen (AOX) by-products which are environmentally undesirable. In addition, the bactericidal efficacy of these materials is substantially reduced in high organic component systems because of rapid reactions of free halogen with organic materials. In high organic component recirculating waters such as pulp and paper processing and oil field applications, these deleterious effects are pronounced.

U.S. Pat. No. 3,328,294 teaches reaction of sulfamic acid with hypochlorite solutions, forming N-chlorosulfamate solutions which are used to disinfect paper-processing streams. The stated advantage is reduced reactions with paper-processing components. Enhanced biocidal efficacy is demonstrated over a non-oxidizing biocide containing N-methyldithiocarbamate and cyanodithioimidocarbonate with bacterial concentrations of  $10^3$  cfu/ml being achieved at residual chlorine concentrations of 1.6 ppm as  $\text{Cl}_2$ . Unfortunately, as a practical matter, N-chlorosulfamic acid provides reduced biocidal efficacy relative to hypochlorite, thus limiting its usefulness as a papermaking slimicide.

U.S. Pat. No. 3,749,672 teaches the use of N-hydrogen materials to formulate bleaching solutions with enhanced stability to spontaneous decomposition. The claimed formulations contain (A) a hypohalite, (B) an N-hydrogen compound, (C) N-halo relation product of (A) with (B) at concentrations of  $1.0 \times 10^{-3}$  to 1.0 molar, and (D) a buffer to maintain pH 4-11. The preferred compositions are liquid formulations containing a phosphate buffer, sulfamic acid and sodium hypochlorite buffered at pH 10. Use of such formulations containing the N-hydrogen compound is discussed, as is fighting microorganisms in paper mills. The essence of the invention is the production of stable formulations which can be handled and shipped without the loss of active halogen. This is effected by the incorporation of a buffer. The invention is not concerned with the on-site combination of hypochlorite-containing solutions or process streams with N-hydrogen compounds, but only with shelf-stable formulations.

While this patent teaches reduced yellowing when the formulations are used as bleaches, neither the reduction of AOX nor the unexpected biocidal activity enhancement of active halogen by N-hydrogen compounds in pulp slurries is revealed.

## BRIEF DESCRIPTION OF THE INVENTION

It has been discovered that selected N-hydrogen compounds and their chlorinated derivatives, such as 5,5-dimethylhydantoin (DMH), dramatically improve the bactericidal efficacy of hypochlorite solutions in pulp slurries, significantly reducing the amount of hypochlorite required to achieve biological control. Minimization of chlorine usage reduces the predisposition for AOX formation, as well as enhancing cost-effectiveness.

The efficacy is believed to result from the conversion of free halogen to combined halogen by DMH. DMH effectively increases the lifetime of active halogen, thereby

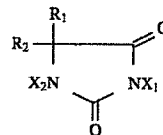
2

increasing biocidal efficacy. Such action increases cost effectiveness and reduces AOX formation.

In contrast to the teaching of U.S. Pat. No. 3,749,672, the subject invention avoids the need to preformulate the constituents off-site and to buffer the solution. On-site formulation of active halogen:N-hydrogen mixtures allows for site-specific stoichiometric optimization in the system recirculation water. The relative stabilities of active halogen and N-hydrogen compounds in recirculation systems is site-specific, since they depend on such factors as composition, temperature, and degree of recycle. Modification of the active halogen:N-hydrogen ratio is not possible with the preformulated solutions of the prior art. Secondly, on-site formulation eliminates the expense and burdens of adding a buffer.

In another embodiment of the instant invention, it has been discovered that certain halogenated N-hydrogen compounds per se also serve as outstanding slimicides for the treatment of circulating water containing organic matter such as in the pulp and paper industry. These compounds show enhanced efficacy over the hypochlorite in these applications. This result is particularly surprising since organic matter, generally over 0.2 wt. % and frequently over 0.5 wt. %, would be expected to interfere with the biocidal efficacy of such compounds. Typically these processing streams have from 0.2 to 3 wt. % organic matter, most frequently from 0.5 to 2 wt. %, comprised of approximately 95-99% pulp fiber as well as additional materials such as sizing rosin and starch.

The N-halohydantoin compounds useful in this embodiment of the invention have the formula:



$\text{R}_1$  and  $\text{R}_2$  are independently selected from hydrogen and alkyl groups (having from 1 to 12 carbons), and  $\text{X}_1$  and  $\text{X}_2$  are independently selected from bromine, chlorine and hydrogen, at least one of  $\text{X}_1$  and  $\text{X}_2$  being halogen, with the proviso that, when  $\text{X}_1$  or  $\text{X}_2$  is bromine,  $\text{R}_1$  is methyl and  $\text{R}_2$  is ethyl. In preferred embodiments,  $\text{R}_1$  is methyl and  $\text{R}_2$  is either methyl or ethyl. Preferred halohydantoins include 1,3-dichloro-5,5-dimethylhydantoin; 1-chloro-5,5-dimethylhydantoin; and dibromo- and bromochloroethylmethylhydantoins; and combinations of these derivatives. Another preferred embodiment includes a mixture of chloro derivatives of 5-ethyl-5-methylhydantoin, such as the mixtures currently sold under the trade name Dantochlor®. The amount of the N-halohydantoin compound used in the recirculating water is broadly from 0.2 to 30 ppm, preferably from 0.5 to 5.0.

## DETAILED DESCRIPTION OF THE INVENTION

The effective form of combined halogen can be generated: a) in situ by the addition of hydantoin to pulp slurries prior to or shortly after hypochlorite injection, b) by mixing DMH and free chlorine solutions prior to pulp slurry injection, or c) by direct feeding of halogenated hydantoins.

In addition to DMH, other N-hydrogen compounds, analogously to DMH, may be used. These include 5,5-dimethylhydantoin, glycouril, sulfamide, trisulfamide,

3

p-toluene-sulfonamide, melamine, sodium triamidometa-phosphate, 5,5-alkylhydantoin, methanesulfonamide, bar-bituric acid, 5-methyluracil, imidazoline, pyrrolidone, aceta-nilide, acetamide, N-ethylacetamide, phthalimide, benzamide, succinimide, cyanamide, urea, N-methylolurea, N-methylurea, acetylurea, biuret, methyl allophanate, methyl carbamate, phthalohydrazide, pyrrole, indole, forma-mide, N-methylformamide, dicyandiamide, ethyl carbam-ate, 1,3-dimethylbiuret, methyl phenyl biuret, 4,4-dimethyl-2-oxazolidinone, 6-methyluracil, 2-imidoazolidone, ethylene urea, 2-pyrimidone, N-ethylacetamide, azetidin-2-one, 2-pyrrolidone, caprolactam, phenyl sulfinimide, phenyl sulfinimidyldiamide, diphenyl sulfonimide, dimethyl sulfin-imine, isothiazolene-1,1-dioxide, orthophosphoryl triamide, pyrophosphoryl triamide, phenyl phosphoryl-bis dimethyl amide, boric acid amide, hydantoin, and pyrrole. Expressly excluded is sulfamic acid, as its properties have been found to be inadequate for the purposes of the invention.

DMH and cyanuric acid enhance efficacy; however, the latter does not mitigate halogen consumption as well as DMH. While all N-hydrogen compounds (e.g., hydantoin, glycouril, sulfonamides, imides, oxazolidinones, amides, amino acids) appear to enhance free halogen efficacy and mitigate halogen consumption to varying degrees, the sul-famic acid described in U.S. Pat. No. 3,328,294 is clearly inferior to the compounds claimed herein. Hydantoin and cyanuric acid are preferred.

A wide variety of "free halogen sources" can be improved by applying the teaching of the instant invention. These include alkali metal and alkaline earth metal hypochlorites such as the lithium, sodium, potassium, calcium, and mag-nesium compounds, chlorine gas, bromine, bromine chlo-ride, halogenated cyanurates such as trichlorocyanuric acid and sodium dichlorocyanurate, and dihalogenated hydanto-ins, and mixtures of such with sodium bromide.

The optimum amount of the N-hydrogen compound used is that needed to convert all free halogen to the combined form. This corresponds to a 1:1 molar ratio of halogen (based on the moles of free halogen) to hydantoin; however, concentrations as low as those producing a 2.6:1 halogen to DMH ratio have been shown to be effective. Any amount of N-hydrogen compound should provide some level of effi-cacy enhancement, while greater amounts of hydantoin do not reduce biocidal efficacy. A range corresponding to 0.1:1 to 10:1 halogen to N-hydrogen compound ratio broadly covers the invention. Halogen to DMH ratios of 0.1:1 to 10:1 correspond to hydantoin dosages of from 0.02 to 180 ppm.

Typically active halogen concentrations of 0.1–10 ppm as  $\text{Cl}_2$  are employed in the pulp media. Amounts of 1 to 3 ppm are preferred.

To more fully describe the subject invention, attention is directed to the following examples:

#### EXAMPLE 1

The addition of 5,5-dimethylhydantoin (DMH) to sodium hypochlorite solutions enhances the biocidal activity of sodium hypochlorite. The conditions of this experiment were a modification of ASTM E 600-91. Two biocide solutions were evaluated: NaOCl and NaOCl mixed with DMH in a 0.25:1 molar ratio. The NaOCl and the DMH were mixed prior to pulp introduction. The biocides were intro-duced to the pulp slurry 10 minutes prior to inoculation with  $2 \times 10^6$  cfu/ml *P. Aeruginosa* and *E. Aerogenes*. The pulp slurry consisted of 1.3% ground aspen wood pulp and 200 ppm rosin adjusted to pH=5.0–5.5 with aluminum sulfate.

4

Bacteria populations were measured 3 hours after pulp slurry inoculation. Final total halogen concentrations were measured at the time of bacterial population plating by sample centrifuging followed by standard DPD analyses. Biocides were neutralized with sodium thiosulfate prior to plating. The results are set forth in Table 1:

TABLE 1

Effect of DMH on NaOCl/Bactericidal Efficacy					
System	Sample	Total Halogen: (ppm as $\text{Cl}_2$ )		% Residual Halogen	Final Bacteria (cfu/ml)
		Initial	Final		
NaOCl	A	10	0.08	0.8	$\leq 10^3$
	B	7.5	0.04	0.5	$\leq 10^3$
	C	5.0	0.00	0	$\leq 10^3$
	D	3.0	0.00	0	$10^4$
	E	1.0	0.00	0	$10^5$
NaOCl: DMH (0.25:1 mole ratio)	F	10	5.2	52	$\leq 10^3$
	G	7.5	4.1	55	$\leq 10^3$
	H	5.0	2.8	56	$\leq 10^3$
	I	3.0	1.1	37	$10^3$
	J	1.0	0.5	50	$\leq 10^3$

DMH significantly enhanced the bactericidal efficacy of NaOCl. In the presence of DMH 1 ppm halogen produced bacteria reduction equivalent to that of 5 ppm halogen when used alone. This is a fivefold increase in efficacy.

DMH also reduced active halogen loss, reducing the predisposition for AOX formation. In the absence of DMH essentially all active halogen was consumed, while up to 56% remained when the DMH was present.

#### EXAMPLE 2

NaOCl efficacy was also enhanced by DMH upon NaOCl addition to DMH-treated slurries. Prereaction of DMH with NaOCl as described in Example 1 was not required. The conditions of this experiment were in other respects the same as Example 1. The molar ratio in the pulp slurry was 1:1 NaOCl to DMH. The results are reported in the table below:

TABLE 2

Effect of DMH-Treated Pulp on NaOCl/Bactericidal Efficacy					
System	Sample	Total Halogen: (ppm as $\text{Cl}_2$ )		% Residual Halogen	Final Bacteria (cfu/ml)
		Initial	Final		
NaOCl	A	15	0.11	0.7	$<10^3$
	B	10	0.04	0.4	$<10^3$
	C	7.5	0.06	0.5	$<10^3$
	D	5	0.02	0.4	$10^4$
	E	3	0.00	0.0	$10^5$
NaOCl: DMH (1:1 mole ratio)	F	1	0.00	0.0	$10^6$
	G	15	1.88	12.5	$<10^3$
	H	10	0.88	8.8	$<10^3$
	I	7.5	0.41	5.5	$<10^3$
	J	5	0.16	3.2	$<10^4$
	K	3	0.05	1.7	$10^4$
	L	1	0.00	0.0	$10^6$

Again bactericidal efficacy was significantly increased by the presence of DMH. In the presence of DMH a 2 log reduction in bacteria concentration was achieved with an initial halogen concentration of 3 ppm, while 5 ppm was required in its absence: a twofold increase in efficacy.

The consumption of active halogen by the pulp medium was again mitigated by the presence of DMH.

5

## EXAMPLE 3

DMH efficacy enhancement against preinoculated samples was also demonstrated. The conditions were the same as Example 1 except that the pulp was inoculated with bacteria 5 minutes prior to biocide introduction as opposed to 10 minutes after. Also the NaOCl to DMH mole ratio was increased from 0.25:1 to 1:1. The results are shown in Table 3:

TABLE 3

Effect of DMH on NaOCl Bactericidal Efficacy in Preinoculated Samples				
Pulp Slurry Bactericidal Efficacy				
System	Total Halogen (ppm as Cl <sub>2</sub> )		% Residual Halogen	Final Bacteria (cfu/ml)
	Initial	Final		
NaOCl	16.3	0.34	2.1	<10 <sup>3</sup>
	3.4	0.03	1.0	<10 <sup>3</sup>
	0.8	0.01	1.3	10 <sup>6</sup>
NaOCl:	15.0	3.6	24	<10 <sup>3</sup>
(1:1 mole	3.2	1.5	47	<10 <sup>3</sup>
ratio)	0.8	0.3	38	10 <sup>3</sup>

DMH again enhanced efficacy. In its presence a 3 log reduction was effected at a dosage of 0.8 ppm halogen (as compared to no reduction at 0.8 ppm in its absence). Active halogen consumption was again mitigated in the presence of DMH.

## EXAMPLE 4

The effectiveness of DMH to mitigate halogen consumption was demonstrated at NaOCl to DMH molar ratios of 0.6:1 to 2.6:1. The experimental conditions were the same as those of Example 2, except that the pulp slurry was not inoculated with bacteria. The results are shown in the table below:

TABLE 4

Effect of NaOCl:DMH Molar ratio on Halogen Consumption			
NaOCl:DMH Mole Ratio	Total Halogen (ppm as Cl <sub>2</sub> )		% Residual Halogen
	Initial	Final	
0	25.6	0.11	0.4
2.6:1	25.6	6.4	25
1.3:1	25.6	7.6	30
0.6:1	25.6	7.5	29

DMH concentrations as low as those producing NaOCl to DMH ratios of 2.6:1 reduced pulp slurry halogen consumption. As bactericidal efficacy of DMH treated systems was observed to correlate with residual total halogen concentration (see Examples 1 and 2), DMH is expected to enhance hypochlorite biocidal activity at DMH concentrations at least as low as those which provide NaOCl to DMH ratios of 2.6:1.

## EXAMPLE 5

The activity of hydantoins was demonstrated to be greater than sulfamic acid and similar to cyanuric acid. The conditions were the same as those of Example 1. The molar ratio of the NaOCl to N-hydrogen compound was 1:1. The results are shown in Table 5:

6

TABLE 5

Effect of Cyanuric Acid, Sulfamic Acid and MEH on Bactericidal Efficacy					
System	Sample	Total Halogen: (ppm as Cl <sub>2</sub> )		% Residual Halogen	Final Bacteria (cfu/ml)
		Initial	Final		
NaOCl	5099:46	5.0	0.03	0.6	10 <sup>5</sup>
	A	3.0	0.02	0.7	10 <sup>5</sup>
	B	1.0	0.00	0.0	10 <sup>6</sup>
NaOCl:	C	5.0	3.8	76	10 <sup>5</sup>
Sulfamic	D	3.0	2.5	83	10 <sup>5</sup>
Acid	E	1.0	0.6	60	10 <sup>6</sup>
NaOCl:	F	5.0	0.21	4.2	10 <sup>3</sup>
Cyanuric	G	3.0	0.03	1.0	10 <sup>3</sup>
Acid	H	1.0	0.00	0.0	10 <sup>6</sup>
NaOCl:MEH	I	5.0	2.4	48	10 <sup>3</sup>
	J	3.0	0.2	7	10 <sup>4</sup>
	K	1.0	0.03	3	10 <sup>5</sup>

Sulfamic acid produced no efficacy enhancement over sodium hypochlorite alone. In contrast, 5-ethyl-5-methylhydantoin (MEH) dramatically increased NaOCl efficacy, providing a 3 log reduction at 5 ppm halogen as opposed to a 1 log reduction in its absence. Cyanuric acid provided similar efficacy enhancement to MEH.

Of the two components which provided efficacy enhancement, MEH and cyanuric acid, MEH provided the greatest mitigation of halogen decomposition; thus it is expected that MEH would provide the greatest reduction in AOX formation. In this aspect MEH would be preferred over cyanuric acid.

## EXAMPLE 6

The conditions in this experiment were the same as in Example 1 except the initial total halogen concentration with respect to typical microbiological concentration was increased to about 70 ppm as Cl<sub>2</sub> to produce detectable levels of AOX. The results are shown in Table 6:

TABLE 6

Effluent AOX Analyses		
Composition	Initial Total Halogen (ppm as Cl <sub>2</sub> )	Effluent AOX (ppm)
NaOCl	74	5.8
NaOCl:DMH	69	3.7

DMH reduced the AOX of NaOCl-treated pulp slurry effluent by 36%.

## EXAMPLE 7

This example shows the surprising efficacy of an N-halohydantoin compound as a bactericide as compared to the conventionally used sodium hypochlorite. Specifically, Dantochlor®, a commercial halogenated hydantoin containing predominantly dichlorodimethylhydantoin and dichloroethylmethylhydantoin was used. The conditions were the same as those of Example 1. Table 7 shows the results:

TABLE 7

Efficacy of N-Halohydantoin Compound		
	Total Halogen: (ppm as Cl <sub>2</sub> )	Final Bacteria
	% Residual	

System	Sample	Initial	Final	Halogen	(cfu/ml)
NaOCl	I	7.5	0.05	1	$\leq 10^3$
	J	5.0	0.02	0.4	$\leq 10^3$
Dantochlor	K	3.0	0.00	0	$10^6$
	E	7.5	4.2	56	$\leq 10^3$
	F	5.0	3.4	68	$\leq 10^3$
	G	3.0	1.1	36	$\leq 10^3$
	H	1.0	0.83	83	$\leq 10^3$

As can be seen from the data, Dantochlor showed a fivefold efficacy increase over sodium hypochlorite, providing a greater than 3 log reduction at 1 ppm initial halogen compared to 5 ppm for sodium hypochlorite. Additionally, the consumption of active halogen by the pulp medium was much less where the Dantochlor was used relative to sodium hypochlorite.

What is claimed is:

1. A method of enhancing the efficacy of a free halogen-generating slimicide and reducing organic halogen by-products in an organic matter-containing circulating water system which comprises adding an N-hydrogen compound selected from the group consisting of p-toluene-sulfonamide, dimethylhydantoin, methylethylhydantoin, cyanuric acid, succinimide, urea, 4,4-dimethyl-2-oxazolidinone, and glycouril, directly to said system before or after the addition of the slimicide or with said slimicide in a mixture consisting essentially of the slimicide and said compound; wherein the N-hydrogen compound is added at a ratio sufficient to maintain a 0.1:1 to 10:1 mole ratio of slimicide to N-hydrogen compound in the circulating system, wherein at least 0.2 weight percent of said organic matter is present in said system, wherein the slimicide is chlorine gas, bromine, bromine chloride, an alkali metal or alkaline earth metal hypochlorite, a halogenated hydantoin, a halogenated cyanurate, or halogenated cyanuric acid, and wherein said mixture of the N-hydrogen compound and the slimicide is present in said system in a slimicidally effective amount.

2. The method of claim 1 wherein the mixture of the slimicide and the N-hydrogen compound is formed just prior to the addition to said circulating water system.

3. The method of claim 1 wherein the slimicide is chlorine gas or sodium hypochlorite.

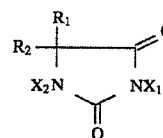
4. The method of claim 1 wherein from 0.1 to 10 ppm of active slimicide (expressed as  $\text{Cl}_2$ ) is maintained in the circulating water system.

5. The method of claim 1 wherein the circulating water system is used in pulp and paper processing or oil field applications.

6. The method of claim 1 wherein said organic matter is present in said system at from about 0.5 to about 3 weight percent.

7. The method of claim 1 wherein said organic matter is from about 95 to about 99 percent wood fiber.

8. The method of claim 1 wherein said slimicide is a halogenated hydantoin of the formula:



wherein  $R_1$  and  $R_2$  are independently selected from the group consisting of lower alkyl having 1 to 12 carbon atoms, and wherein  $X_1$  and  $X_2$  are independently selected from the group consisting of bromine, chlorine and hydrogen, and at least one of  $X_1$  and  $X_2$  being bromine or chlorine.

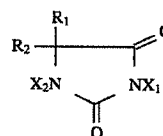
9. The method of claim 8 wherein said organic matter is from about 95 to about 99 percent wood fiber.

10. The method of claim 8 wherein said organic matter is present in said system at from about 0.5 to about 3 weight percent.

11. The method of claim 8 wherein the halogenated hydantoin contains bromochlorodimethylhydantoin.

12. The method of claim 8 wherein the halogenated hydantoin is a mixture of dichlorodimethylhydantoin and dichloroethylmethylhydantoin.

13. A method of enhancing the efficacy of a free halogen-generating slimicide and reducing organic halogen by-products in an organic matter-containing circulating water system which comprises adding an N-hydrogen compound selected from the group consisting of p-toluene-sulfonamide, dimethylhydantoin, methylethylhydantoin, cyanuric acid, succinimide, urea, 4,4-dimethyl-2-oxazolidinone, and glycouril, directly to said system before or after the addition of the slimicide or with said slimicide in a mixture consisting essentially of the slimicide and said compound; wherein the N-hydrogen compound is added at a ratio sufficient to maintain a 0.1:1 to 10:1 mole ratio of slimicide to N-hydrogen compound in the circulating system; and wherein at least 0.2 weight percent of said organic matter is present in said system, wherein said slimicide is a halogenated hydantoin of the formula:



wherein  $R_1$  and  $R_2$  are independently selected from the group consisting of lower alkyl having 1 to 12 carbon atoms, wherein  $X_1$  and  $X_2$  are independently selected from the group consisting of bromine and chlorine, and wherein the mixture of the N-hydrogen compound and the slimicide is present in said system in a slimicidally effective amount.

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# APPENDIX

## K



Solutions! March 2003

## Combined halogens: new products to combat an old problem, Solutions!, Online Exclusives, March 2003



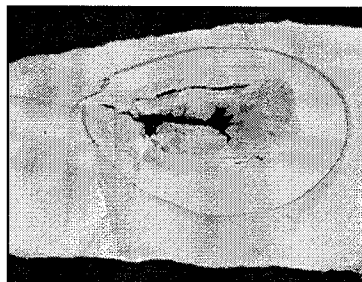
### Combined halogens: New products to combat an old problem

By Bruce Urtz, Ondeo Nalco Company

*New combined halogen products offer papermakers several potential advantages over the use of traditional oxidants in the battle against slime.*

As long as papermakers have been making paper, microorganisms have been interfering with the process. Microorganisms such as bacteria and fungi are capable of forming slime on the paper machine and other areas, such as the saveall. Slime can create various problems such as sheet defects, holes, breaks, and plugged shower nozzles or screens. **Figure 1** illustrates a sheet hole caused by slime.

One way papermakers have controlled slime is through the use of oxidants. Products like bleach (sodium hypochlorite), sodium hypobromite (activated bromide), and chlorine dioxide have been around for many years. These oxidants can be relatively inexpensive, and very effective against slime-producing organisms. However, the use of oxidants does not come without problems. Oxidants can be corrosive, damage felts, and react with various papermaking chemistries—for instance, optical brighteners and dyes.



**Figure 1.** Sheet hole caused by slime.

Over the past several years, a number of new oxidant products have entered the marketplace. These products consist of halogens, bromine and/or chlorine, combined with an organic or inorganic carrier. One key advantage to combining the halogen is that it can often reduce the negative impact of the oxidant while maintaining its biocidal properties.

#### **An old idea**

The idea of combining a halogen with another molecule so that the halogen is less aggressive but still biocidal is nothing new. In the 1930s and 1940s, mixing bleach (or chlorine gas) with ammonia to make chloramines for microbiological control in papermaking systems was very common (1, 2). Even though chloramine treatment was often touted as being more effective than chlorine, eventually the chemistry was abandoned. Some of the reasons for abandoning chloramine treatment were increased corrosion and increased microbiological activity, presumably due to the ammonia, a good source of nitrogen for bacteria (3, 4). In the 1960s and 1970s, bleach in combination with sulfamic acid (chlorosulfamate) was proposed as a biocide with low reactivity to process equipment and chemistries (5, 6). However, the product never obtained commercial success in paper probably due to the weak biocidal activity of chlorosulfamate.

#### **Many shades, but only a few colors**

In the past several years, interest in using combined halogens has been rejuvenated. Papermakers are currently using a number of combined halogen products for microbiological control in papermaking systems (7, 8, 9, 10). The various trade names often make it confusing to determine the number and nature of the products available. In reality, papermakers currently use only four types of chemistries: hydantoin, sulfamate, ammonia/ammonium, and isocyanurate.

**Hydantoin:** This group consists of bromine, chlorine, or both attached to a hydantoin molecule. Halohydantoins are not very stable in liquid form so they are manufactured and sold as a solid product either as powder, granules, or briquettes. Feeding halohydantoins requires the use of a powder feeder or a brominator. A brominator consists of a vessel with granules or briquettes. Water flows through the vessel, dissolves product, and is sent to the process. Powder feeders work by making a slurry and delivering that slurry to the process. Once in the process, the product completely dissolves.

**Sulfamate:** This group consists of bromine or chlorine attached to a sulfamate molecule. Unlike the halohydantoins, halosulfamates can be manufactured as stable liquid products. Currently, only bromosulfamate

is used for paper mill water treatment. Chlorosulfamate is used in some cooling tower applications.

**Ammonia/ammonium:** Haloamines can be generated by mixing chlorine or bleach with ammonia or an ammonium salt. The two can be mixed in the process water or pre-mixed before application to the process water. Like halohydantoin, these types of haloamines cannot be manufactured as stable liquid products. Recently, bleach in combination with ammonium bromide has been introduced as a way to produce a new haloamine oxidant (7).

**Isocyanurate:** This group consists of chlorine attached to an isocyanurate molecule. However, sodium bromide may also be present, allowing for the formation of hypobromite. Like halohydantoin, halocyanurates are produced in solid form. One halocyanurate product, which is applied using a specialized powder feeder, has enjoyed commercial success in cooling tower applications and utilities, but has seen only limited application in paper (9).

#### Potential benefits of combined halogens

**Persistence:** One potential benefit of using a combined halogen is persistence. Oxidants like bleach and sodium hypobromite are quick reacting but usually not persistent. In contrast, combined halogens, in general, are slower acting but more persistent. Since all mills recycle their process water to some extent, persistence can be beneficial. It allows the oxidant to carry farther through the system and provide more long-term control.

Figure 2 provides an example of this. Three oxidants at equal concentration were added separately to white water samples. Every 30 minutes, non-treated white water was added to the treated white water samples to see if any residual oxidant was left to handle the additional microbial challenge. Initially, bleach was the most effective oxidant; however, after several challenges, the combined halogens were found to be more effective due to their persistence.

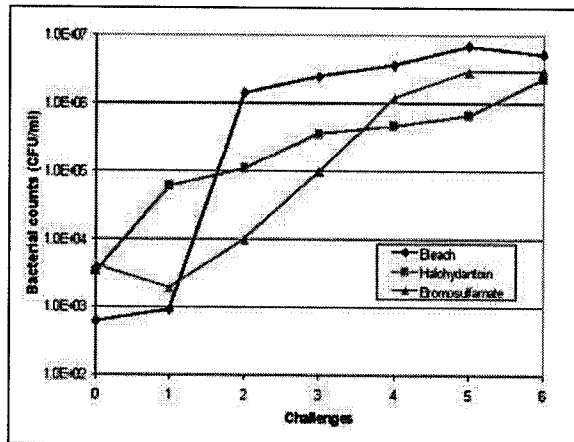


Figure 2. Persistence of halohydantoin and bromosulfamate vs. bleach in white water from an uncoated free-sheet mill. Note how bleach is more effective in controlling bacterial counts initially, but the halohydantoin and bromosulfamate are more effective after repeated challenges.

#### Increased efficacy in high oxidant demand systems:

When oxidants are added to process water, not only do they react with the microorganisms they are supposed to kill, they also

react with the various substances in the process. These other components create an oxidant demand that neutralizes the oxidant and prevents it from being biocidal. Oxidant demand can vary dramatically from mill to mill. One advantage of using a combined halogen is that it may have less reaction with this demand and, therefore, be a more effective biocide than its non-combined counterpart. However, this is not true of all combined halogens, and will vary from mill to mill.

#### Better slime penetration and removal:

What papermakers refer to as slime, microbiologists refer to as biofilms. There is some evidence that combined halogens are more effective at killing bacteria in biofilms than non-combined halogens (11, 12, 13). However, very little work has been done in paper systems, which typically have more complex biofilms due to the presence of other components such as fillers and fibers.

#### Better compatibility with papermaking chemistries:

As stated earlier, one proposed advantage of using a combined halogen is better compatibility with papermaking chemistries. We have conducted a number of experiments in this area looking at various chemistries such as size, wet strength, dyes, and optical brighteners. In general, combined halogens are more compatible than their counterparts, bleach and sodium hypobromite. Still, there are exceptions. For example, the compatibility of three combined halogens was tested on an optical brightener (Figure 3). Two of the combined halogens were less reactive than bleach and sodium hypobromite. The third, a halohydantoin, was more reactive than bleach. Therefore, you cannot assume that a combined halogen is always going to be more compatible than its non-combined counterpart.

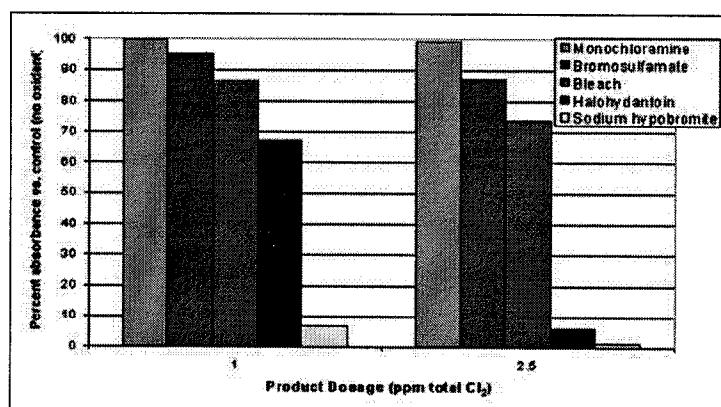


Figure 3. Effect of various oxidants on an optical brightener.

*Better compatibility with papermaking equipment: If combined halogens are more compatible with papermaking chemistries, you might expect that this would be true for equipment as well. In our laboratory, as well as others, we have found that combined halogens such as bromosulfamate and halohydrantoin are more compatible with felt fibers than bleach or sodium hypobromite (14). However, when we looked at the effect on vapor phase corrosion, the results were mixed (Figure 4).*

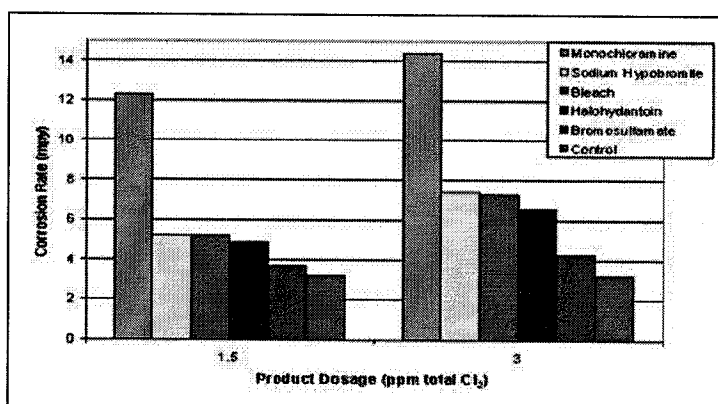


Figure 4. Effect of various oxidants on vapor phase corrosion of mild steel.

*In the case of monochloramine, a haloamine we found it to be more corrosive than other oxidants including bleach and sodium hypobromite. This is likely due to the high volatility of chloramines. Therefore, as with chemistry compatibility, you cannot always assume that a combined halogen is more compatible than a non-combined one.*

#### At what cost?

*For papermakers, one of the biggest concerns is cost. Oxidants like bleach are commodity chemicals; as such, they are relatively inexpensive. Combined halogens are more expensive. However, in weighing the economics of the application, one has to consider the hidden or not so hidden costs of oxidant application. This can include dye and optical brightener consumption, corrosion, and felt damage. Also, if the combined halogen is more effective on an active basis than its non-combined counterpart, the cost difference is reduced.*

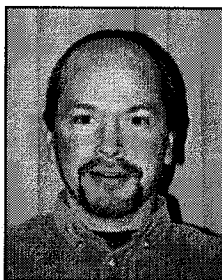
*Another potential drawback of using combined halogens is feeding and controlling dosages. Most combined halogen products discussed here require some sort of specialized feeding equipment. Controlling the dosage of some of these products can be challenging, especially the solid products.*

#### Choosing the right product

*Combined halogens are no different than other biocides in that there is no "one size fits all" product. Therefore, it is important to understand not only the oxidant, but also the mill in which it will be applied. Screening the product is essential. If the screening results look good, other factors should be considered. For example, is there concern about optical brightener destruction, dye consumption, or corrosion? In 1929 when discussing the use of chlorine, C. M. Baker came to the conclusion that "...owing to differences in the conditions in different mills, each mill is a separate problem and should be studied individually" (15). The same holds true more than 70 years later when applying a combined halogen.*

**About the Author:**

Bruce Urtz is a Senior Research Microbiologist, Paper Services Division, for Odeco Nalco Company. He holds a Ph. D. in Microbiology from North Carolina State University and has worked for Odeco Nalco for 5 and 1/2 years.



**Acknowledgements**

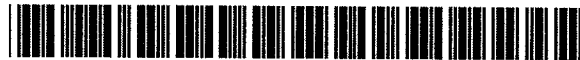
The author wishes to acknowledge Dr. Michael Enzien for his help on the corrosion testing.

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# APPENDIX

## L



US006478972B1

(12) **United States Patent**  
**Shim et al.**

(10) **Patent No.:** **US 6,478,972 B1**  
(45) **Date of Patent:** **Nov. 12, 2002**

(54) **METHOD OF CONTROLLING MICROBIAL FOULING**

(75) Inventors: **Sang Hea Shim, Seoul; Chung Soo Kim, Kyungki-do, both of (KR)**

(73) Assignee: **Acculab Co., Ltd., Seoul (KR)**

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/605,398**

(22) Filed: **Jun. 28, 2000**

(30) **Foreign Application Priority Data**

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Jun. 12, 2000 (KR) ..... 2000-32103

(51) Int. Cl.<sup>7</sup> ..... **C02F 1/76**

(52) U.S. Cl. .... **210/755; 162/161; 210/756; 210/764; 422/37; 424/661; 424/723**

(58) Field of Search ..... **210/698, 752, 210/754, 755, 756, 764; 162/161; 422/37; 424/661, 723**

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*Primary Examiner*—Peter A. Hruskoci

(57) **ABSTRACT**

A method of controlling microbial fouling is provided.

The method controls microbial fouling using hypobromous acid, HOBr, formed by the reaction between an aqueous solution of alkali or alkaline earth metal hypochlorite and a bromide ion source.

The method is characterized in that the alkali or alkaline earth metal hypochlorite or/and the bromide ion source is/are stabilized by the addition of a stabilizer before the hypobromous acid is formed by the reaction there between.

**19 Claims, No Drawings**

## METHOD OF CONTROLLING MICROBIAL FOULING

This application claims priority to Korean patent application No. 1999-57299 filed Dec. 13, 1999 and No. 2000-32103 filed Jun. 12, 2000.

### 1. Field of the Invention

The present invention relates to a method of controlling microbial fouling and a control system therefor, more specifically a method of controlling microbial fouling using bromination method wherein hypobromous acid, HOBr, formed by the reaction between hypochlorous acid and bromide ion, is used for controlling the microbial fouling in aqueous system, and a control system therefor.

### 2. Background of the Invention

In aqueous system such as cooling water towers, industrial water system, paper processing water and oil field waters, microorganisms including bacteria, fungi and algae may cause biological problems including microbiologically influenced corrosion. In addition, the microorganisms form slime. These microbiologically influenced corrosion and slime formation may deteriorate structures, reduce cooling efficiency, change colors as well as increase environmental and health problems.

Generally, methods using oxidizing biocides and non-oxidizing biocides have been used to control microbial fouling in aqueous systems,

Oxidizing biocides sterilize microorganisms by oxidizing cell proteins while non-oxidizing biocides sterilize microorganisms by inhibiting metabolism.

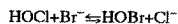
Examples of such non-oxidizing biocides include isothiazolone, methylenebisocyanate, glutaraldehyde, quarternary ammonium, and the like.

Generally the biocidal power of nonoxidizing biocides is not comparable with that of oxidizing biocides, but the biocidal activity of non-oxidizing biocides lasts longer than that of oxidizing biocides. The method using oxidizing biocides includes chlorination method and bromination method, and each reaction mechanism is as follows:

#### Chlorination



#### Bromination



The produced HOCl and OCl<sup>-</sup> in chlorination, and HOBr and OBr<sup>-</sup> function as biocides. In chlorination, the concentration of HOCl and OCl<sup>-</sup> vary depending on pH. As pH increases, the concentration of HOCl decrease more rapidly than that of OCl<sup>-</sup> as HOCl is more effective as a biocide than OCl<sup>-</sup>, the chlorination becomes less effective in the system having the pH higher than 7. Further in chlorination method, the ammonia or amine compound contained in an aqueous system such as cooling water may react with HOCl or OCl<sup>-</sup> to form chlorinated amines which is less effective as biocide, resulting in a reduction of biocidal power.

On the other hand, in bromination method, the concentration of HOBr can still be maintained even in high pH system, and thus, the biocidal power is not reduced. Further the brominated amine formed by the reaction with ammonia in aqueous system exerts almost same biocidal power as HOBr. Thus the bromination method is effective compared to the chlorination method.

As a HOCl or OCl<sup>-</sup> source in both method, alkali or alkaline earth metal hypochlorites, for example sodium hypochlorite (NaOCl) are widely used to control microbial fouling in various kinds of aqueous system including cooling water towers, bleaching process, swimming pools, petroleum industry. However, the alkali or alkaline earth metal hypochlorite is not stable under typical storage conditions and several methods have been suggested to stabilize NaOCl. One of them was suggested in U.S. Pat. No. 3,328,294 to Self. The '294 patent teaches to stabilize the unstable NaOCl by reacting with an equal molar ratio of sulfamic acid.

Hypobromite having various advantages over hypochlorite such as better biocidal performance in high pH or amine environments and lower volatility also have the unstable problems under typical storage conditions.

U.S. Pat. No. 5,795,487 (corresponding to Korea Patent Applications number 97-708350) (hereinafter referring to as simply '487 patent) assigned to NALCO Chemical Company disclosed a process to manufacture stabilized alkali or alkaline earth metal hypobromite.

The method comprises the steps of mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source; allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form unstable alkali or alkaline earth metal hypobromite; and adding to the unstable solution of alkali or alkaline earth metal hypobromite an alkali metal sulfamate as stabilizer.

In the '487 patent, the inventors emphasized that the surprisingly increased stability of the stabilized sodium hypobromite achieved by patent method is basically due to the specific order of reagent addition in the process of manufacture, that is, in the order of an aqueous solution of alkali or alkaline earth metal hypochlorite, a water soluble bromide ion source and an aqueous solution of an alkali metal sulfamate. In addition, '487 patent teaches that addition of the stabilizer prior to bromide oxidation would not permit the formations of NaOBr because NaOBr is synthesized by the reaction formula  $\text{NaOCl} + \text{NaBr} \rightarrow \text{NaOBr} + \text{NaCl}$ .

However since in the '487 patent the aqueous solution of hypochlorite reacts with an equal molar ratio of the bromide ion source which is expensive on the basis of the above reaction formula, the method according to the '487 patent is costly and requires continuous supply of bromide ion source to maintain the biocidal power in the system.

An object of the present invention is to provide an economic method of controlling microfooling in aqueous system using a stabilized hydrobromite.

Another object of the present invention is to provide an efficient method of controlling microfooling in aqueous system having low volatility, a high free halogen residual long-lasting biocidal power.

It is an object of the present invention to provide a method for preparing a stabilized aqueous alkali or alkaline earth metal hydrobromite solution to be used for the above method.

Further another object of the present invention is to provide an improved anti-microfooling system.

### SUMMARY OF THE INVENTION

We have been studying an efficient method of controlling microbiofouling in aqueous system using an aqueous hypochlorite solution, water soluble bromide ion source, metal sulfamate as stabilizer, and unexpectedly found that addition of the stabilizer prior to bromide oxidation could permit the formation of NaOBr, which is contrary to the teaching of the '487 patent.



3

Specifically, soon after the stabilizer has been added to an aqueous solution of alkali or alkaline earth metal hypochlorite prior to the formation of hypobromite (NaOBr), the stabilized hypochlorite did not react with the water soluble bromide ion source and thus did not allow the NaOBr formation, which met with the teaching of the '487 patent. However it has been surprisingly found that several to several tens hours after the stabilized hypochlorite and bromide ion source have been added to into aqueous system, the concentration of free halogen residual begun to dramatically increase and the biocidal power lasted long.

Based on the above discovery the inventors continued to study and completed the present invention.

The main feature of the present invention is to allow hypochlorous acid, HOCl, to react with a stabilizer before hypobromites have been formed by the reaction between the hypochlorous acid and a water soluble bromide source in controlling microbial fouling in aqueous system using hypobromite produced by the reaction of hypochlorite and bromide ion source.

In one embodiment of the invention, when alkali or alkaline earth metal hypochlorite is used as a hypochlorous acid source, it is preferred to stabilize the hypochlorite by reacting with a stabilizer and then to allow the stabilized hypochlorite to contact a water soluble bromide ion source to form hypobromites.

However since the hypochlorites preferentially react with the stabilizer than with the bromide ion source, the hypochlorite, the stabilizer and the bromide ion source may simultaneously be added to an aqueous system to be treated. Also it may be acceptable to mix the stabilizer with the bromide ion source first, and then to allow the mixture to contact the hypochlorite to form hypobromite.

The main features of the present invention is not to allow hypochlorites to react with a water soluble bromide ion source before the hypochlorite has been stabilized.

Such characteristic features of the present invention is definitely distinguished from those of the '487 patent wherein an aqueous solution of alkali or alkaline earth metal hypochlorite is allowed to react with a water soluble bromide ion source to form unstabilized solution of alkali or alkaline earth metal hypobromite, and the addition of stabilizer is followed.

Resultantly the present invention has various advantages over the '487 patent such as less consumption of bromide ion source which is expensive.

Gaseous chlorine can also be used in the present invention as a hypochlorous acid source.

A first aspect of the present invention provides a method for controlling microbial fouling using hypobromous acid, HOBr, formed by the reaction between hypochlorous acid and a bromide ion source, wherein the method comprises the steps of stabilizing the hypochlorous acid by reacting with a stabilizer and then allowing the stabilized hypochlorous acid to react with a water soluble bromide ion source to form hypobromous acid.

A second aspect of the present invention provides a method of controlling microbial fouling in aqueous system comprising:

- (a) mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent of active chlorine with a stabilizer selected from the group consisting of amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acid, amino acid, sulfuric acid, phosphoric acid and boric

4

acid in a molar ratio of stabilizer to alkali or alkaline earth metal hypochlorites of from 1:9 to 9:1 to form a stabilized alkali or alkaline earth metal hypochlorites: and

- (b) consecutively or simultaneously applying the stabilized alkali or alkaline earth metal hypochlorites formed in the above step (a) and a water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid, and mixtures thereof into a locus of microorganism to protect.

The stabilized alkali or alkaline earth metal and the bromide ion source can be applied to the microorganism locus in a quantity to maintain the level of free halogen residual within a range between 0.05~10 ppm.

A third aspect of the present invention provides a method of controlling microbial fouling in aqueous system which comprises:

- (a) preparing on aqueous solution of alkali or alkaline earth metal hypochlorites having from about 5 percent to about 70 percent of active chlorine;
- (b) mixing a water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid and mixture, thereof, and a stabilizer selected from the group consisting of amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acid, amino acid, sulfuric acid, phosphoric acid, and boric acid to prepare a mixture of bromide ion source and stabilizer; and
- (c) consecutively or simultaneously applying the aqueous solution of alkali or alkaline earth metal hypochlorites prepared in the above step (a) and the mixture of bromide ion source and stabilizer into a locus of microorganism to protect in a quantity to maintain the level of free halogen residual within a range between 0.05~10 ppm

A fourth aspect of the present invention provides an anti-microbial fouling system comprising: an aqueous solution pack of stabilized alkali or alkaline earth metal hypochlorite including an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 to 70% of active chlorine and an aqueous solution of stabilizer selected from the group consisting of urea, thioureas, creatinine, cyanuric acids, alkyl hydantoins, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine in a quantity to provide a molar ratio of stabilizer to alkali or alkaline earth metal hypochlorite of 1:9~9:1; and a pack containing water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid and mixtures thereof.

A fifth aspect of the present invention provides an anti-microbial fouling system comprising: a first pack containing an aqueous solution of alkali or alkaline earth metal hypochlorites having about 5~70% of active chlorine, and a second pack containing a mixture of stabilizer selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkylhydantoins, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine, and water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid and the mixture thereof, and wherein the molar ratio of the stabilizer to the alkali or alkaline earth metal hypochlorite is 1:9~9:1.

A sixth aspect of the present invention provides an anti-microbial fouling system prepared by: forming an aqueous

5

ous solution of stabilized hydrochlorite by adding to an aqueous solution of alkali or alkaline earth metal hydrochlorite a stabilizer selected from the group consisting of amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acids, amino acids, sulfuric acid, phosphoric acid and boric acid in a sufficient amount to stabilize the aqueous solution of alkali or alkaline earth metal hypochlorite; and then adding to the stabilized hydrochlorite a bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid with the molar ratio of the bromide ion source to the stabilized hydrochlorite being in a range between 1/10-1.

A seventh aspect of the present invention provides a method of controlling microbial fouling which comprises: applying an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 to 70 percent of active chlorine, a stabilizer selected from the group consisting of urea, thiourea, creatinines cyanuric acids, alkylhydantions, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine in an amount to provide a molar ratio to the alkali or alkaline earth metal hypochlorite of 1:9-9:1, and a water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid and mixture thereof into a locus of microorganism to protect, in a quantity to maintain the level of free halogen residual within a range between 0.05-10 ppm, in the order that the stabilizer is applied first to the locus or is applied between the application of the aqueous solution of alkali or alkaline earth metal hypochlorite and the water soluble bromide ion source or is applied simultaneously with the aqueous solution of alkali or alkaline earth metal hydrochlorite and the water soluble bromide ion source.

A eighth aspect of the present invention provides a method of controlling microbial fouling which comprises: applying gaseous chloride, a stabilizer selected from the group consisting of urea, thioureas, creatinine, cyanuric acids, alkylhydantions, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine, and a water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid and mixtures thereof, into a locus of microorganisms in a quantity to maintain the level of free halogen residual within a range between 0.05-10 ppm, in the order that the stabilizer is applied first to the locus or is applied between the application of the gaseous chlorine and the water soluble bromide ion source or is applied simultaneously with the gaseous chlorine and the water soluble bromide ion source.

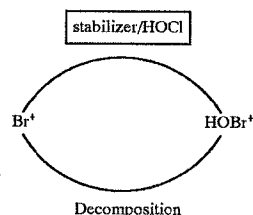
#### DETAILED DESCRIPTION OF THE INVENTION

The first aspect of this invention provides a method for controlling microbial fouling using hypobromous acid (HOBr) formed by the reaction between hypochlorous acid (HOCl) and a water soluble bromide ion source ( $\text{Br}^+$ ), characterized in that an aqueous solution of alkali or alkaline earth metal is stabilized with adding a stabilizer before hypobromous acid is formed by the reaction between the hypochlorous acid and the bromide ion source,

The above characteristic features of this invention distinguish from the '487 patent wherein an aqueous solution of alkali or alkaline earth metal hypochlorite is allowed to react first with a water soluble bromide ion source to form unstabilized solution of alkali or alkaline earth metal hypobromide, and then the addition of stabilizer is followed.

6

In the present invention wherein hypochlorous acid is stabilized by the addition of the stabilizer and after that the bromide ion source is added to the stabilized hypochlorous, the stabilized hypochlorous acid is believed to function as a reservoir to provide  $\text{Br}^+$  ion from the bromide ion source with HOCl in order to form HOBr which sterilizes microorganism in an aqueous system to protect and is decomposed by ultraviolet rays and recycled for further use as schematically shown below.



Thus according to the present invention the expensive bromide compound is consumed in a small quantity, while in the prior art the expensive bromide compound is consumed in a large quantity since an aqueous solution of hypochlorite reacts with an equal molar ratio of a bromide ion source on the basis of the formula  $\text{NaOCl} + \text{NaBr} \rightarrow \text{NaOBr} + \text{NaCl}$ .

As previously discussed, according to the present invention the addition of the stabilizer to the hypochlorous acid should be carried out prior to bromide oxidation, which has never been disclosed or taught in any prior arts including '487 patent.

In other words, prior arts including '487 patent is based on the fixed idea that already stabilized hypochlorous acid (hypochlorites) do not react with bromine ion, while the present invention is based on the findings that already stabilized hypochlorous acid reacts with bromine ion several to several tens hours after they have been applied into an aqueous system to protect depending on the temperature of the system and the biocidal activity lasted long time.

Actually the inventors found that hypobromous acid was formed several hours after at a system temperature of 35° C., and 24 hours after at room temperature.

As hypochlorous acid sources, alkali or alkaline earth metal hypochlorites may be preferably used in the present invention. Gaseous chlorine may also be used as a hypochlorous acid source.

To form hydrochlorous acid, gaseous chlorine or alkali/alkaline earth metal hypochlorites may be introduced into the aqueous system to treat or protect to react with water.

The second aspect of the present invention provides a method of controlling microbial fouling in aqueous system, characterized in that the method comprising mixing a specific aqueous solution of alkali or alkaline earth metal hypochlorites as hypochlorous acid source with specific stabilizers to prepare stabilized hypochlorites, and then consecutively or simultaneously applying the stabilized hypochlorites and bromide ion source into a locus of microorganism to protect.

This aspect of the present invention, as is in the first aspect, also has advantages over the prior art such as less consumption of expensive bromide ion source, long-lasting biocidal activity.

Characteristic features of the third aspect of the present invention is to mix stabilizer with bromide ion source

instead of mixing with aqueous solution of alkali or alkaline earth metal hypochlorites in the second aspect. Namely, according to the method of the second aspect, the hypochlorites is stabilized with stabilizer before bromide ion source is added, but in the third aspect bromide ion source is mixed with stabilizer and the mixture and hypochlorites is consecutively or simultaneously applied into a locus of microorganism to protect.

In this case, when the hypochlorites is applied into a aqueous system, the stabilizer in the mixture preferentially react with the hypochlorite to form stabilized hypochlorite which results in same effect as in the second aspect.

The fourth aspect of the present invention provides an anti-microbial fouling system comprising a first pack containing an aqueous solution of stabilized hypochlorite and a second pack containing bromide ion source.

The characteristic features of the fifth aspect is to mix stabilizer with bromide ion in a pack.

The sixth aspect of the present invention provides an anti-microbiofouling system which enables to storage the stabilized hypochlorite and the bromide ion source in a pack.

Even when the stabilized hypochlorite and bromide ion source are stored in same pack in concentrate state, the chlorites and bromide ion source do not react each other so long as they are stored in a pack in concentrate state. However when the stabilized hypochlorite and bromide ion source are introduced into a dilute aqueous system of microorganism locus, they begin to react to form hypobromous acid having biocidal activity.

The seventh aspect of the present invention provides a method of controlling microbial fouling, comprising applying an aqueous solution of hypochlorites, stabilizer and bromide ion source in a specific order.

With specifying the order of addition (application), direct reaction between unstabilized hypochlorites and bromide ion source could be prevented, and the stabilization of hypochlorites is preceded,

In the eighth aspect of the present invention, gaseous chlorine is used as an hypochlorous acid source.

When gaseous chlorine is introduced into a locus of microorganism, the gaseous chlorine reacts with water to form hypochlorous acid.

Each component used in this invention will be discussed hereinafter.

The alkali or alkaline earth metal hypochlorite which is useful in this invention is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite and calcium hypochlorite.

The alkali or alkaline earth metal hypochlorite preferably contains about 5-70% of chlorine as active halogen.

The hypochlorite having less than 5% of chlorine is commercially invalid and the hypochlorite having more than 70% of chlorine is hard to commercially manufacture.

The bromide ion source useful in this invention is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide and hydrobromic acid. In a preferred embodiment, the bromide ion source is sodium bromide.

The stabilizer in this invention includes amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acid, amino acid, sulfuric acid, phosphoric acid, and boric acid.

Examples of those stabilizer are urea, thiourea, creatinine, cyanuric acids, alkyl hydantoin, mono- or di-ethanolamine,

organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine. Sulfamic acid is preferred from the economic and efficiency view point.

The amount of hypochlorite used will vary depending upon the kinds of hypochlorite used and the degree and extent of contaminated by microbial fouling. When an aqueous system is severely contaminated, the initial quantity of hypochlorite is preferably increased. The molar ratio of the stabilizer to the alkali or alkaline earth metal hypochlorite is 1:9 to 9:1.

And the amount of bromide ion source used to the stabilized hypochlorite will vary depending upon the degree and extent contaminated by microorganism. A typical molar ratio of bromide ion source to the stabilized hypochlorite is 1/10-1 mol.

For example, when the concentration of the stabilized hypochlorite is 10 ppm, the concentration of the bromide ion source could be no less than 1 ppm. Therefore the expensive bromide ion source, in the present invention, is less consumed than in the prior arts wherein equal molar ratio of the expensive bromide ion source to the hypochlorite is required.

Though the concentrations of the stabilized hypochlorites and the bromide ion source in aqueous system to protect vary depending on the aqueous system, the level of free halogen residual in the system is preferably between 0.05-10 ppm, more preferably between 0.1-5 ppm, and most preferably 0.2-2 ppm.

The anti-microbial fouling system according to the present invention may contain any of the conventional corrosion and scale inhibitors known in the art.

The corrosion inhibitor includes anodic corrosion inhibitor such as chromates, nitrites, orthophosphates, silicates and molybdates, cathodic corrosion inhibitor such as zinc, polyphosphates, and phosphonates, and copper corrosion inhibitor such as mercaptobenzothiazole, benzotriazole and tolytriazole. The scale inhibitor includes organo phosphates and acrylic polymers.

Examples of the organo phosphates include trethanolamine phosphate (TEAP), aminotris(methylene phosphonic acid) (AMP), 1-hydroxyethylidene-1,1-bisphosphonic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

The acrylic polymer may include homo-acrylic polymer, co-acrylic polymer and ter-acrylic polymer.

The method and system according to this invention can be widely applied to any aqueous system where inhibition of the growth of microorganism is required.

The aqueous system include, but are not limited to: cooling water tower, air cleaner, swimming pool, spas, industrial water system, laundry detergents, bleaching agent, oil field water, sweet water, gas scrubber system, recycling water system and water slide.

Any conventional pH modifier can be added to the aqueous solution of alkali or alkali earth metal hypochlorites and may include, but are not limited to, sodium hydroxide, potassium hydroxide, magnesium hydroxide, lithium hydroxide and calcium hydroxide.

The following examples are presented to illustrate further various aspect of the present invention, but are not intended to limit the scope of this invention in any aspect.

#### EXAMPLE 1

##### Free Halogen Residual

Sample 1 to 3 was added into an aqueous system in an amount of 5 ppm based on NaOCl and the change of free halogen residual concentration in the system was measured for 8 days.

Results of the tests are shown below table 1.

TABLE 1

Sample No.	days							
	1	2	3	4	5	6	7	8
1*	0.04	0.11	0.03	0.02	0.04	0.03	0.02	0.02
2*	0.67	0.77	0.65	0.24	0.07	0.03	0.03	0.02
3*	0.16	2.34	1.70	1.62	1.12	0.73	0.43	0.05

Sample 1\*: sulfamic acid was added into NaOCl solution

Sample 2\*: equal molar ratio of NaOCl and NaBr were mixed and followed by addition of sulfamic acid, as suggested in '487 patent

Sample 3\*: same amount of NaOCl as in sample 1 and 2 was mixed with sulfamic acid, and the mixture was applied into an aqueous system to protect, and addition of same amount of NaBr as in sample 2 was followed

As shown in the Table 1, the stabilized NaOCl(sample 1) released few free halogen residual. And sample 2 prepared by the method suggested by '487 patent showed high concentration of free halogen residual until 2nd day after but the concentration was rapidly decreased from 3rd day.

Sample No 3 prepared by the method according to the present invention showed low concentration of free halogen residual on the first day of addition, however from the second day the concentration of free halogen residual was dramatically increased and lasted to the 7th day.

These results demonstrate high efficiency of the method and system of this invention. With the same molar ratio and components, the higher concentration of free halogen residual was accomplished and it lasted longer than 2 times compared to the prior art.

The concentration of free halogen residual in the present invention was changed from 2.34(second day) to 0.43(7th day), while in the '487 patent from 0.77 to 0.03. Thus the present invention requires less consumption of expensive bromide ion source than required by the prior art, and additionally more improved performance due to higher concentration can be attained.

#### EXAMPLE 2

##### Activity Against Microorganism

Tests were conducted to determine the activity of the inventive system and method against bacteria. To polluted water containing 103 bacteria were added 10 ppm of sample 4 and 5 based on NaOCl, respectively. After 48 hours, 20 ppm of sample 4 and 5 were additionally added and concentrations of free halogen residual and the number of bacteria alive were measured.

Results of this test are shown below.

TABLE 2

		UNIT: ppm days					
Sample No.		1	2	3	4	5	6
Sample 4*	Halogen residual	0.33	0.03	0.16	0.11	0.14	0.09
	No. of bacteria	10 <sup>2</sup>	10 <sup>2</sup>	10 <sup>1</sup>	10 <sup>1</sup>	10 <sup>2</sup>	10 <sup>2</sup>
Sample 5*	Halogen residual	0.05	0.08	0.14	0.73	0.67	0.28
	No. of bacteria	10 <sup>4</sup>	10 <sup>3</sup>	10 <sup>2</sup>	10 <sup>1</sup>	10 <sup>0</sup>	10 <sup>0</sup>

Sample 4: sulfamic acid was introduced after NaOCl and NaBr were mixed according to the teachings of '487 patent

TABLE 2-continued

Sample No.	UNIT: ppm days					
	1	2	3	4	5	6

Sample 5: According to the present invention, NaOCl was mixed with sulfamic acid, and then the mixture was introduced to the aqueous system to be treated.

After that, equal amounts of NaBr to the sample 4 were added into the aqueous system

As table 2 shows, Sample No. 4 prepared by the teaching of '487 patent had better biocidal power on the same day the mixture was introduced, compared to sample 5 prepared according to the present invention. But 24 hours later, the biocidal power was suddenly decreased and even on the sixth day formation of mess was visually observed in the aqueous system.

On the other hand, Sample No. 5 prepared according to the present invention continuously demonstrated long-lasting and better anti-fouling activities. No moss was visually found in the aqueous system.

#### EXAMPLE 3

##### Efficiency Against Moss

To polluted water in which algae were floating were added sample 6 and 7 in an amount to provide each 20 ppm concentration.

The concentration of free halogen residual and the condition of algae in the polluted aqueous system were observed.

The change of free halogen concentration is set forth in Table 3.

TABLE 3

sample no	UNIT: ppm days					
	1	2	3	4	5	6
6	0.98	0.74	0.35	0.12	0.07	0.03
7	0.24	2.12	2.42	1.48	1.28	1.16

Sample 6: Sulfamic acid was introduced after NaOCl and NaBr were mixed, according to the teachings of '487 patent

Sample 7: According to the present invention, NaOCl was mixed with sulfamic acid and then the mixture was introduced into the aqueous system to be treated.

After that, equal amount of NaBr to the sample 4 were added into the aqueous system.

As shown in Table 3, the concentration of free halogen of the sample No. 6 prepared by the teaching of '487 patent has been suddenly decreased. The floating algae were deposited at the bottom and cohesive slime was begun to form. With the lapse of time, the algae color was changed from light yellowish green to dank green. The number of bacteria was decreased for the first 13 days, but rapidly increased thereafter.

However, Sample No. 7 according to the present invention, prepared by first mixing NaOCl and sulfamic acid to form stabilized NaOCl, applying the stabilized NaOCl to a aqueous system to protect, and then adding NaBr to the system, demonstrated long-lasting biocidal activities and higher biocidal power than in Sample No. 6. Algae was deposited at the bottom, as was in Sample No. 6, but has not grown any longer, and disappeared 5 days later, bacteria was not observed from 3 days after.

After 30 days storage, very strong slime plugs were formed in sample 6, while any slime has not been found in sample 7.

11

In addition, Sample No. 6 demonstrated less-effectiveness for algae than for bacteria and fungus.

## EXAMPLE 4

Effects of NaBr Amount on Free Halogen Residual Concentration

NaOCl was stabilized with sulfamic acid and the stabilized NaOCl was introduced into an aqueous system to be treated and then to the aqueous system was added NaBr. The change of concentration of free halogen residual depending on the NaBr amount added has been observed for 7 days after the addition.

The data appears in Table 4, below.

TABLE 4

amount of each component				
		sample 8	sample 9	sample 10
Component	NaOCl	10 ppm	10 ppm	10 ppm
	Sulfamic acid	10.92 ppm	10.92 ppm	10.92 ppm
	NaBr	13.93 ppm	9.69 ppm	4.14 ppm

Concentration of Free Halogen Residual (ppm)				
Time Lapsed				
1 day	0.16	0.09	0.05	
2 days	2.04	1.08	0.64	
3 days	2.12	2.62	2.4	
4 days	2.42	1.66	1.52	
5 days	1.48	1.46	1.24	
6 days	1.28	1.26	1.12	
7 days	1.16	1.11	0.92	

The above Table 4 shows that, according to the present invention, the concentration can be maintained even when the amount of NaBr is decreased. Thus, the amount of expensive bromide ion source can be reduced while maintaining the concentration of free halogen residual.

We claim:

1. A method for controlling microbial fouling comprising introducing hypobromous acid(HOBr), formed by the reaction between hypochlorous acid from a hypochlorous acid source and a bromide ion from a water soluble bromide ion source, to an aqueous system where inhibition of the growth of microorganism is required, which comprises the step of first stabilizing the hypochlorous acid by reacting with a stabilizer, and then allowing the stabilized hypochlorous acid to react with the water soluble bromide ion source to form said hypobromous acid, to maintain a level of free halogen residual in said system to control said microbial fouling.

2. The method according to claim 1, wherein the hypochlorous acid source is selected from the group consisting of gaseous chlorine and aqueous solution of alkali or alkaline earth metal hypochlorites.

3. The method according to claim 2, wherein the hypochlorous acid source is an aqueous solution of alkali or alkaline earth metal hypochlorite.

4. The method according to claim 1, wherein the hypochlorous acid source is an aqueous solution of alkali or alkaline earth metal hypochlorite, and the stabilizer is added into the aqueous solution of alkali or alkaline earth metal hypochlorite, and the stabilized alkali or alkaline earth metal hypochlorite solution and the water soluble bromide ion source or a mixture of the bromide ion source and the stabilizer are consecutively or simultaneously applied to the aqueous system.

12

5. The method according to claim 4, wherein the stabilizer is added into the aqueous solution of alkali or alkaline earth metal hypochlorite to form a stabilized alkali or alkaline earth metal hypochlorite, and so formed stabilized alkali or alkaline earth metal hypochlorite and the water soluble bromide ion source are consecutively or simultaneously applied to the aqueous system.

6. The method according to claim 4, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, and the bromide ion source is sodium bromide.

7. The method according to anyone of claims 4 and 5, the aqueous system is a cooling water tower, an air cleaner, a swimming pool, a spas, an industrial water system, a laundry detergents, a bleaching agent, a recycling water system, an oil field water, a sweet water, a gas scrubber system or a water slide.

8. The method according to any one of claims 2 to 5, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, calcium hypochlorite and mixtures thereof.

9. The method according to claim 1, wherein the bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hydrobromic acid, and mixtures thereof.

10. The method according to claim 1, wherein the stabilizer is selected from the group consisting of amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acid, amino acid, sulfuric acid, phosphoric acid and boric acid.

11. The method according to claim 10, wherein the stabilizer is selected from the group consisting of urea, thiourea, creatinines, cyanuric acids, alkyl hydantoins, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine.

12. The method according to claim 11, wherein the stabilizer is sulfamic acid.

13. A method of controlling microbial fouling in aqueous system comprising:

(a) mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent of active chlorine with a stabilizer selected from the group consisting of amide derivatives of carbonic acid, hydrogen cyanide, carboxylic acid, amino acid, sulfuric acid, phosphoric acid, and boric acid in a molar ratio of stabilizer to alkali or alkaline earth metal hypochlorite of from 1:9 to 9:1 to form stabilized alkali or alkaline earth metal hypochlorite; and

(b) consecutively or simultaneously applying the stabilized alkali or alkaline earth metal hypochlorite formed in the above step (a) and a water soluble bromide ion source selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, hypobromic acid and mixtures thereof to the aqueous system in a quantity to maintain the level of free halogen residual within a range between 0.05-10 ppm.

14. The method according to claim 13, wherein the alkali or alkaline earth metal hypochlorite is mixed with the stabilizer in a molar ratio of 1:1.

15. The method according to claim 13, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, calcium hypochlorite, and mixtures thereof.

16. the method according to claim 13, wherein the stabilizer is selected from the group consisting of urea, thiourea,

**13**

creatinones, cyanuric acids, alkyl hydantoins, mono- or di-ethanolamine, organic sulfonamides, biuret, sulfamic acid and salts thereof, organic sulfamic acid and melamine.

17. The method according to anyone of claims 13 to 16, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, and the bromide ion source is sodium bromide, and the stabilizer is sulfamic acid.

18. The method according to anyone of claims 13 to 16, wherein the aqueous system is a cooling water tower, an air

**14**

cleaner, a swimming pool, a spas, an industrial water system, a laundry detergents, a bleaching agent, a recycling water system, an oil field water, a sweet water, a gas scrubber system or a water slide.

19. The method according to claim 13, the concentration of free halogen residual in the aqueous system is within a range between 0.2~2 ppm.

\* \* \* \* \*

# APPENDIX

## M

## **DECLARATION OF B. GARY McKINNIE**

I, B. Gary McKinnie, declare as follows:

### **I. GENERAL BACKGROUND**

1. My educational background is as follows:

I received a B.S. degree in Chemistry from Northeast Louisiana University, Monroe, Louisiana in 1969. I received a Ph.D. in Organic Chemistry from Louisiana State University, Baton Rouge, Louisiana in 1975. I pursued post-doctoral studies from August 1975 to August 1976 at the University of Georgia, Athens, Georgia and from August 1976 to April 1977 at the University of Illinois, Champaign-Urbana, Illinois.

2. My work history is as follows:

I was employed by Ethyl Corporation ("Ethyl") starting in 1977. When Ethyl divested itself of Albemarle Corporation ("Albemarle"), I joined Albemarle and I have been employed by Albemarle continuously to the present time.

3. I have held various technical titles within Ethyl / Albemarle Corp. (Chemist, Senior chemist, Specialist, Senior Specialist, Advisor, Senior Advisor) and in 2000 was promoted to Distinguished Advisor.
4. Since 1983 I have conducted research and development of processes for producing bromine, brominated flame retardants and other bromine-related products. Since 2000 I have carried out research and development work on processes for making bromine-based biocides.
5. A list of my patents and publications is appended hereto as Appendix A.

### **II. MATERIAL COMMON TO ALL THREE INTERFERENCES**



- d. Accordingly, the two moles of hydroxide would be neutralized by the  $H^+$  generated by HBr dissociation and acidic N-hydrogen dissociation.
- e. Support for the impossibility of practicing claim 25 using an acidic halogen stabilizer can be found in Example III of the '267 patent specification, which indicates that even at a molar ratio of approximately 1:1:3, the pH of the mixed solution was less than 13 (specifically, 12.5).

**EXHIBIT 1017**, col. 6, l. 65-col. 7, l. 12.

47. It would be impossible to prepare a "caustic solution" called for in claims 14-15 and 25 of the '267 patent if an alkaline earth metal hydroxide is used as the only hydroxide source.

- a. As noted above, the "caustic solution" prepared in step 1 has a pH higher than 14.
- b. The low solubility of alkaline earth metal hydroxides in water makes it impossible to produce an aqueous solution having a pH greater than or equal to 13 when alkaline earth metal hydroxide is the only hydroxide source.

iii. Method 3 (Claims 27-28 of the '267 Patent)

48. The portions of the '267 patent specification at col. 3, ll. 25-45 and col. 7, ll. 27-45 relate to Method 3, the subject of the processes recited in claims 27-28. **EXHIBIT 1017**.

49. The theoretical maximum N-bromo compound, calculated as active bromine content in parts per million (wt/wt) for an aqueous formulation produced using Method 3,

a. U.S. Patent No. 3,558,503 (Goodenough *et al.*)

96. U.S. Patent No. 3,558,503 (hereafter, the “Goodenough *et al.*”) teaches preparation of novel bromine solutions and processes for preparing them that are resistant to degradation and/or decomposition of the bromine values contained therein (**EXHIBIT 1003**, column 1, line 13-22).
97. Goodenough *et al.* claims an aqueous bromine solution comprising from about 0.01 to about 100,000 parts per million by weight bromine values wherein the bromine stabilizer is biuret, succinimide, urea and lower aliphatic mono- and disubstituted ureas containing 2-4 carbon atoms in each substituent group, sulfamic acid, and a subgenus of alkyl sulfonamides. **EXHIBIT 1003**, col. 5, ll. 21-32. The claimed solutions further contain sufficient alkali or alkaline earth metal hydroxide additive to provide a pH in the range of about 8 to about 10. **EXHIBIT 1003**, col. 5, ll. 32-37.
98. Goodenough *et al.* defines “bromine values” as active oxidizing species including HOBr, BrO<sup>-</sup> and Br<sub>2</sub>. **EXHIBIT 1003**, col. 1, ll. 36-38.
99. The definition used by Goodenough *et al.* for bromine values is the same as that used for the term “active bromine content” in the Moore applications. Thus, for example, a solution having a bromine value of 50,000 according to Goodenough *et al.* is the same as an aqueous solution having an active bromine content of 50,000 ppm according to the Moore applications.
100. Goodenough *et al.* teaches that the order of addition of the three reactants (bromine, halogen stabilizer and metal hydroxide) to water is not critical for producing stablized aqueous bromine solutions. **EXHIBIT 1003**, col. 2, ll. 7-12.

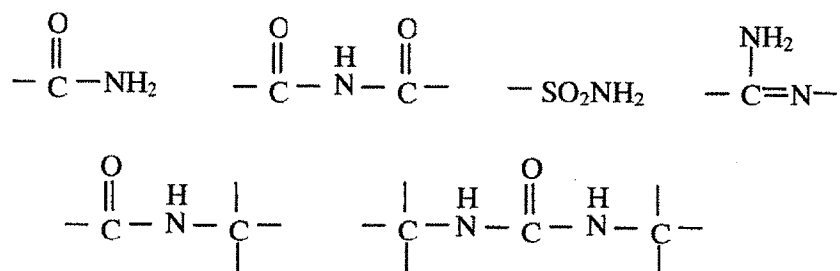
101. The working examples in the Goodenough et al. patent describe only two different orders of addition of the reactants. **EXHIBIT 1003**, Example 3 (col. 4, l. 33- col. 5, l. 15). In the first method the bromine is mixed into an aqueous solution consisting of water, the bromine stabilizer and alkali or alkaline earth metal hydroxide. **EXHIBIT 1003**, Example 3 (col. 4, l. 33- col. 5, l. 15). "Solution A" of Example 3 in the specification was prepared by this method using sulfamic acid as the halogen stabilizer and magnesium hydroxide as the base. **EXHIBIT 1003**, col. 4, ll. 66-69. In the second method, alkali or alkaline earth metal hydroxide is mixed into an aqueous solution containing bromine and the bromine stabilizer. "Solution B" of Example 3 was prepared by this method using sulfamic acid as the halogen stabilizer and magnesium hydroxide as the base. **EXHIBIT 1003**, col. 4, ll. 69-72.
102. Goodenough et al. states that solutions "A" and "B" were stored in brown ultraviolet light-screening bottles. **EXHIBIT 1003**, col. 5, ll. 1-2. Storage in such a bottle indicates an attempt to maximize residual bromine values (see paragraph 15 and 15.a, above), which would have been associated with storage at or below room temperature (see paragraph 16, above). In any event, due to the exothermic nature of bromine addition to alkaline sulfamate solutions, some cooling would necessarily occur, absent storage at an increased temperature. See paragraph 14, above.
103. The bromine values for "Solution A" and "Solution B" differed by only a few percent and were at or below 10,000 ppm. **EXHIBIT 1003**, col. 4, l. 73-col. 5, l. 7.
104. Goodenough et al. does not describe an aqueous bromine solution comprising greater than about 100,000 parts per million by weight bromine values wherein the bromine stabilizer is sulfamic acid.

105. Goodenough et al. does not teach that an aqueous bromine solution comprising greater than about 100,000 parts per million by weight bromine values can be produced using any method described in the '503 patent.
106. I have been asked what the pH of an aqueous sulfamate solution would be prior to bromine addition according to the order of reactant addition used to produce Solution A of Example 3 of Goodenough, wherein the hydroxide source is sodium hydroxide (NaOH), the halogen stabilizer is sulfamic acid, the final pH is between 8-10, and the active bromine content in the final solution is 100,000 ppm. I have also been asked to determine the overall molar ratio of  $\text{Br}_2$ :sulfamic acid:NaOH which would be required to produce these solutions.
- On a theoretical basis, based on the reactions which are believed to occur, one can work backward from the equation used to calculate the theoretical maximum active bromine content.
  - Attached as **Exhibit B (EXHIBIT 1019)** is a table showing the amounts (in grams) of each of the reactants which would be necessary to achieve 100,000 ppm active bromine content assuming 100% yield was achieved. According to the calculations, regardless of the  $\text{Br}_2/\text{N}$  ratio used and the final pH selected, the pH of the aqueous alkali metal sulfamate solution would be around 13.9 prior to bromine addition. **EXHIBIT 1019**, p. 1 and 2, data labeled "pH prior to Bromine addition".
  - The amount of excess NaOH required to achieve a final pH between 8 and 10 is minimal in comparison to the total amount of NaOH required in the reactions. Thus, for a  $\text{Br}_2/\text{N}=2.0$ , the molar ratio is approximately 2:1:3,

regardless of final pH. For a Br<sub>2</sub>/N=1.0, the molar ratio is approximately 1:1:2 (again, regardless of final pH). For a Br<sub>2</sub>/N=0.5, the molar ratio is approximately 1:2:3 (again, regardless of final pH).

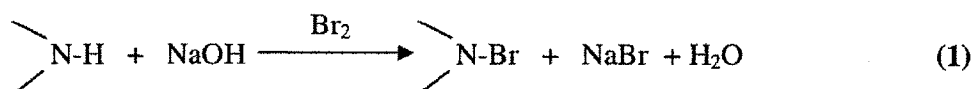
b. U.S. Patent 3,147,259

107. U.S. Patent No. 3,147,259 (hereafter, the "259 patent") teaches a process for preparing N-bromo compounds containing only bromine, from N-hydrogen compounds containing at least one radical selected from the group consisting of



**EXHIBIT 1012**, col. 2, ll. 36-54.

108. As described in the '259 patent, the general prior art method for preparing N-bromo compounds from an N-hydrogen compound containing a primary or secondary amine radical was to add bromine to an aqueous alkaline solution containing the halogen stabilizer. (**EXHIBIT 1012**, col. 1, l. 56-col. 2, l. 3 and col. 2, ll. 36-42).
109. Use of the prior art method to brominate an N-hydrogen compound containing a single secondary amine, amide or imide radical results in an overall reaction as follows:



# APPENDIX

## N

ascribe the difference in reaction enthalpies to a bonding interaction more favorable in  $\text{CuT}^-$  than in  $\text{H}[\text{CuT}]$  compared with the change in overall bonding between  $\text{Cu}(\text{EDTA})^{2-}$  and  $\text{H}[\text{Cu}(\text{EDTA})]^-$ . This might result from a reorientation of metal-ligand bonds in the  $\text{CuT}^-$  species resulting in either release of strain or more effective metal-ligand interaction. Some internal reorientation is consistent with the more negative  $\Delta S^\circ$  value for  $\text{H}[\text{CuT}]$  acidic dissociation compared with that for  $\text{H}[\text{Cu}(\text{EDTA})]^-$ . Both processes restrict internal motion by binding a carboxylate group, but this restriction seems larger in the case of  $\text{H}[\text{CuT}]$ .  $\Delta S^\circ$  for the acidic dissociation reactions consists of contributions from several processes: (1) solvent ordering around  $\text{H}^+$ , common to both reactions; (2) increased secondary solvation around the copper complexes, a process that provides a larger negative contribution to  $\text{H}[\text{Cu}(\text{EDTA})]^-$  dissociation than to  $\text{H}[\text{CuT}]$  dissociation; (3) positive contributions due to solvent release from the sixth copper coordination; (4) loss of internal freedom. Of these factors the last might account for the more negative  $\Delta S^\circ$  value observed for  $\text{H}[\text{CuT}]$  dissociation. That is, differences in solvent binding at the sixth copper coordination site might result in a relatively more negative contribution to  $\Delta S^\circ$  for  $\text{H}[\text{CuT}]$  dissociation. However, the sixth coordination position on  $\text{Cu}^{2+}$  is known to be only weakly solvated so that differences between weakly solvated sites are not

likely to provide for the observed result. Consequently, it appears possible that some distortion of  $\text{Cu}^{2+}$  ligation occurs upon  $\text{CuT}^-$  formation. This proposition seems supported by the X-ray crystallographic data, which indicate an unusually large trigonal distortion in  $\text{CuT}^-$  in which the locus of nitrogen atoms is twisted away from the carboxylate locus by about  $30^\circ$  from the idealized octahedral orientation. A large trigonal distortion of this kind would certainly influence the ligand field near  $\text{Cu}^{2+}$  and might profoundly effect the magnitude of the ligand field, thus accounting for the unusual difference between spectral properties of  $\text{H}[\text{CuT}]$  and  $\text{CuT}^-$ . As a final comparison we note that  $\lambda_{\text{max}} = 660 \text{ nm}^{26}$  for aqueous  $\text{Cu}[\text{9}] \text{aneN}_3^{2+}$ , which we presume exists as a hexacoordinate species. Unfortunately, no crystallographic data is available for this complex. Nevertheless it seems unlikely that large trigonal distortions would be present and that the similar  $\lambda_{\text{max}}$  values of  $\text{H}[\text{CuT}]$  and  $\text{Cu}[\text{9}] \text{aneN}_3(\text{H}_2\text{O})_3^{2+}$  reflect approximately octahedral coordination. Thus, it appears that the large displacement of  $\lambda_{\text{max}}$  from 660 nm for  $\text{H}[\text{CuT}]$  to a value near 750 nm for  $\text{CuT}^-$  results from a substantial distortion of the ligand field in  $\text{CuT}^-$ , which we connect with a release of strain interactions in  $\text{H}[\text{CuT}]$ . The importance of these interactions is consistent with thermodynamic, X-ray crystallographic, and spectral evidence.

Contribution from the Department of Chemistry,  
Purdue University, West Lafayette, Indiana 47907

## Kinetics and Mechanism of General-Acid-Assisted Oxidation of Bromide by Hypochlorite and Hypochlorous Acid

Krishan Kumar and Dale W. Margerum\*

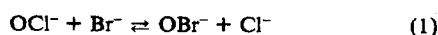
Received March 12, 1987

The rate expression for the oxidation of bromide by  $\text{HOCl}$  and  $\text{OCl}^-$  is  $-\text{d}[\text{OCl}^-]_{\text{T}}/\text{dt} = k_{\text{HA}}[\text{HA}][\text{OCl}^-]_{\text{T}}[\text{Br}^-]$ , where  $[\text{OCl}^-]_{\text{T}} = [\text{OCl}^-] + [\text{HOCl}]$  and  $\text{HA}$  is a general acid ( $\text{H}_2\text{O}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{ClCH}_2\text{COOH}$ , or  $\text{H}_3\text{O}^+$ ). The  $k_{\text{HA}}$  value for  $\text{H}_3\text{O}^+ + \text{OCl}^- + \text{Br}^-$  is  $3.65 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$  (this path requires  $\text{HOCl}$  as an intermediate), while the  $k_{\text{HA}}$  value for  $\text{H}_2\text{O} + \text{HOCl} + \text{Br}^-$  is  $1.32 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ . In terms of second-order expressions, the rate constant for  $\text{HOCl}$  and  $\text{Br}^-$  is  $1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , while the rate constant for  $\text{OCl}^- + \text{Br}^-$  is only  $0.90 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . The proposed mechanism for the acid-assisted reactions (except for  $\text{H}_3\text{O}^+ + \text{OCl}^-$ ) is a simultaneous proton transfer (from  $\text{HA}$  to  $\text{OCl}^-$  or to  $\text{HOCl}$ ) and  $\text{Cl}^+$  transfer to  $\text{Br}^-$  (to give  $\text{BrCl}$ , which reacts rapidly to give  $\text{OBr}^-$  or  $\text{Br}_2$  and  $\text{Br}_3^-$ ). The Brønsted  $\alpha$  value is 0.75 for the reactions of  $\text{HA}$  with  $\text{OCl}^-$  and  $\text{Br}^-$ , and the  $\alpha$  value is 0.27 for the reactions of  $\text{HA}$  with  $\text{HOCl}$  and  $\text{Br}^-$ . The  $\alpha$  values reflect the degree of proton transfer in the transition state.

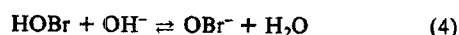
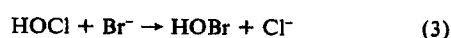
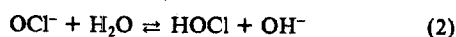
### Introduction

Many non-metal redox reactions take place by atom-transfer or ion-transfer processes. However, much less attention has been paid to the kinetics and mechanisms of these reactions than to electron-transfer reactions. This lack of study may have left the impression that the reactions are well understood. In reality, detailed knowledge of non-metal redox reaction kinetics and mechanisms is limited.

The oxidation of bromide ion by hypochlorite ion was studied by Farkas, Lewin, and Bloch<sup>1</sup> in the pH range 10.8–13.2 under second-order conditions. They verified the stoichiometry of eq 1 and studied the progress of the reaction by titrimetric methods.



They reported the rate-determining step to be the reaction between  $\text{HOCl}$  and  $\text{Br}^-$  with a rate constant of  $2.95 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25  $^\circ\text{C}$ . Their proposed mechanism (eq 2–4) implies nucleophilic



attack by  $\text{Br}^-$  at oxygen, which is equivalent to an  $\text{OH}^+$  transfer between  $\text{Cl}^-$  and  $\text{Br}^-$ .

Recent studies in our laboratory indicate that  $\text{Cl}^+$  transfer occurs in the reactions of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  with iodide<sup>2</sup> and in the reaction of  $\text{NH}_2\text{Cl}$  with sulfite.<sup>3</sup> All of these reactions are general-acid assisted. (General-acid-catalyzed reactions can be considered to be a special case of general-acid-assisted reactions in which no acid is consumed or released.) The reaction of  $\text{OCl}^-$  with  $\text{I}^-$  is also general-acid assisted and appears to have a  $\text{Cl}^+$ -transfer mechanism.<sup>2</sup> We propose  $\text{ICl}$  as an intermediate in all the reactions with iodide. Recent pulsed-accelerated-flow studies<sup>4</sup> show that the reaction between  $\text{ICl}$  and  $\text{I}^-$  to form  $\text{I}_2$  and  $\text{I}_3^-$  is extremely rapid.

Eigen and Kustin<sup>5</sup> determined the kinetics of halogen hydrolysis by temperature-jump relaxation methods. Their work shows that  $\text{H}_3\text{O}^+$  assists the rate of reaction between  $\text{Br}^-$  and  $\text{HOBr}$  to form  $\text{Br}_2$ . Thus,  $\text{H}_3\text{O}^+$  might well be expected to assist the reaction between  $\text{Br}^-$  and  $\text{HOCl}$ , but this has not been studied previously.

In the present work, we report the kinetics of the reaction in eq 1 in base (from 0.45 M  $\text{NaOH}$  to pH 9.5) and show that the

(1) Farkas, L.; Lewin, M.; Bloch, R. *J. Am. Chem. Soc.* 1949, 71, 1988–1991.

(2) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.* 1986, 25, 4344–4350.

(3) Yiin, B. S.; Walker, D. M.; Margerum, D. W., submitted for publication in *Inorg. Chem.*

(4) Margerum, D. W.; Dickson, P. N.; Nagy, J. C.; Kumar, K.; Bowers, C. P.; Fogelman, K. D. *Inorg. Chem.* 1986, 25, 4900–4904.

(5) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* 1962, 84, 1355–1361.

Table I. Absorption Spectral Characteristics of Halogen Species

species	$\lambda_{\max}$ , nm	$\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup>	ref
OCI <sup>-</sup>	292	350	a
OBr <sup>-</sup>	329	345	b
HOCl	230	100	c
HOBr	260	160	b
Br <sub>2</sub>	390	175	b
Br <sub>3</sub> <sup>-</sup>	266	35000	b
BrCl <sub>2</sub> <sup>-</sup>	380	560	d

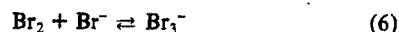
<sup>a</sup>Grey, E. T. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1977. <sup>b</sup>Soulard, M.; Block, F.; Hatterer, A. *J. Chem. Soc. Dalton Trans.* 1981, 2300-2310. <sup>c</sup>Anbar, M.; Dostrovsky, I. *J. Chem. Soc.* 1954, 1105-1108. <sup>d</sup>Reference 7.

Table II. Protonation, Hydrolysis, and Formation Constants

equilibrium	$K$	ref
OCI <sup>-</sup> + H <sup>+</sup> $\rightleftharpoons$ HOCl	$2.75 \times 10^7$	13
OBr <sup>-</sup> + H <sup>+</sup> $\rightleftharpoons$ HOBr	$5 \times 10^8$	5
OCI <sup>-</sup> + H <sub>2</sub> O $\rightleftharpoons$ HOCl + OH <sup>-</sup>	$5.2 \times 10^{-7}$	a
Cl <sub>2</sub> + H <sub>2</sub> O $\rightleftharpoons$ HOCl + H <sup>+</sup> + Cl <sup>-</sup>	$1.0 \times 10^{-3}$	13
Br <sub>2</sub> + H <sub>2</sub> O $\rightleftharpoons$ HOBr + H <sup>+</sup> + Br <sup>-</sup>	$4.4 \times 10^{-9}$	5
Br <sub>2</sub> + Br <sup>-</sup> $\rightleftharpoons$ Br <sub>3</sub> <sup>-</sup>	17	5
BrCl + H <sub>2</sub> O $\rightleftharpoons$ HOBr + H <sup>+</sup> + Cl <sup>-</sup>	$2.95 \times 10^{-5}$	b
H <sub>2</sub> O $\rightleftharpoons$ H <sup>+</sup> + HO <sup>-</sup>	$1.82 \times 10^{-14}$	13

<sup>a</sup>Calculated from  $pK_a$  of HOCl and  $pK_w$  of water. <sup>b</sup>Kanyaev, N.; Shilov, E. A. *Tr. Ivanov. Khim.-Tekhnol. Inst.* 1940, 3, 69.

reaction is general-acid catalyzed. The kinetics of the reaction of HOCl with Br<sup>-</sup> (eq 5 and 6) is studied in acid (from pH 5.3



to 1.0) and is shown to be general-acid assisted. We propose that these reactions occur by transfer of Cl<sup>+</sup> to give BrCl as an intermediate. Bromine chloride is a known compound that can be prepared in nonaqueous solutions by the reaction of *N*-chlorosuccinimide and bromide.<sup>6</sup> In aqueous solutions BrCl is not stable, but in high concentrations of chloride, BrCl<sub>2</sub><sup>-</sup> forms readily.<sup>7</sup>

### Experimental Section

**Reagents.** A 5% (Baker) or 10% (Mallinckrodt) solution of sodium hypochlorite was used as the source of hypochlorite or hypochlorous acid. Stock solutions of hypochlorite were standardized by the measurement of the absorbance of OCI<sup>-</sup> at 292 nm (Table I) or by the formation of I<sub>3</sub><sup>-</sup> ( $\lambda_{\max}$  = 353 nm,  $\epsilon$  = 26 400 M<sup>-1</sup> cm<sup>-1</sup>)<sup>8</sup> after the addition of excess iodide and acid. Solutions of sodium bromide (MCB) were standardized by argentimetric titrations<sup>9</sup> with 5% potassium chromate as an indicator.

Sodium perchlorate, prepared from Na<sub>2</sub>CO<sub>3</sub> and HClO<sub>4</sub>, was used to maintain the ionic strength of the solutions at  $\mu$  = 0.5 M. Reagent grade acids, bases, and buffers were used. Distilled deionized water was used for the preparation of solutions. All solutions were freshly prepared to avoid any complication due to decomposition of hypochlorite or hypochlorous acid. The distribution of protonated, unprotonated, and hydrolyzed species was calculated from the equilibrium data given in Table II.

**Methods.** Absorbance measurements were made with a Perkin-Elmer Model 320 spectrophotometer interfaced to a Perkin-Elmer 3600 data station. Solution pH values were measured with a Corning Model 476051 combination glass electrode and an Orion Model 601 pH meter. All pH values were corrected to give  $-\log [H^+]$  values at 25.0 °C and  $\mu$  = 0.5 M, based on the electrode titrations with standard solutions of NaOH and HClO<sub>4</sub>. Gran plots<sup>10</sup> were used in the calibration of the electrodes.

All reactions were run under pseudo-first-order conditions with Br<sup>-</sup> in large excess. In base, the rates of the reaction were monitored by the disappearance of OCI<sup>-</sup> at 292 nm with the Perkin-Elmer spectrophotometer. Reactions were followed for at least 4 half-lives, and 250 data

Table III. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorite in Base<sup>a</sup>

NaOH Solutions		
[Br <sup>-</sup> ], M	[OH <sup>-</sup> ], M	$k_{\text{obsd}}$ , s <sup>-1</sup>
0.100	0.450	$(1.90 \pm 0.01) \times 10^{-4}$
0.100	0.350	$(2.09 \pm 0.01) \times 10^{-4}$
0.100	0.300	$(2.41 \pm 0.01) \times 10^{-4}$
0.100	0.250	$(2.65 \pm 0.01) \times 10^{-4}$
0.020	0.0972	$(2.12 \pm 0.08) \times 10^{-4}$
0.030	0.0972	$(2.57 \pm 0.01) \times 10^{-4}$
0.200	0.0972	$(1.87 \pm 0.01) \times 10^{-3}$
0.010	0.0493	$(1.731 \pm 0.003) \times 10^{-4}$
0.020	0.0493	$(2.705 \pm 0.004) \times 10^{-4}$
0.080	0.0493	$(1.28 \pm 0.01) \times 10^{-3}$
0.100	0.0493	$(1.42 \pm 0.01) \times 10^{-3}$
0.150	0.0493	$(2.037 \pm 0.001) \times 10^{-3}$
0.200	0.0493	$(2.738 \pm 0.002) \times 10^{-3}$
0.250	0.0493	$(3.14 \pm 0.01) \times 10^{-3}$
0.020	0.0756	$(1.942 \pm 0.002) \times 10^{-4}$
0.020	0.0256	$(5.783 \pm 0.003) \times 10^{-4}$
0.020	0.0106	$(1.278 \pm 0.003) \times 10^{-3}$
0.020	0.0056	$(2.410 \pm 0.002) \times 10^{-3}$

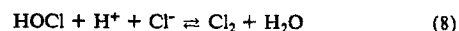
Buffer Solution <sup>b</sup>			
[Br <sup>-</sup> ], M	$-\log [H^+]$	[buffer] <sub>T</sub> , M	$k_{\text{obsd}}$ , s <sup>-1</sup>
0.020	10.99	0.025 (P)	0.016 $\pm$ 0.001
0.050	10.99	0.025 (P)	0.035 $\pm$ 0.005
0.080	10.99	0.025 (P)	0.055 $\pm$ 0.002
0.100	11.01	0.025 (P)	0.066 $\pm$ 0.001
0.120	10.99	0.025 (P)	0.091 $\pm$ 0.005
0.150	10.99	0.025 (P)	0.107 $\pm$ 0.005
0.050	10.97	0.0125 (P)	0.0305 $\pm$ 0.0006
0.050	11.01	0.050 (P)	0.043 $\pm$ 0.001
0.050	11.01	0.0625 (P)	0.045 $\pm$ 0.002
0.100	9.48	0.005 (C)	1.6 $\pm$ 0.1
0.100	9.45	0.0125 (C)	1.88 $\pm$ 0.03
0.100	9.46	0.025 (C)	2.05 $\pm$ 0.03
0.100	9.46	0.0375 (C)	2.02 $\pm$ 0.08
0.100	9.48	0.0625 (C)	2.03 $\pm$ 0.07
0.100	9.48	0.075 (C)	2.25 $\pm$ 0.07
0.100	9.48	0.100 (C)	2.54 $\pm$ 0.07

<sup>a</sup>[OCI<sup>-</sup>] = 6.00  $\times$  10<sup>-4</sup> M,  $\mu$  = 0.5 M (NaClO<sub>4</sub>), 25.0 °C,  $\lambda$  = 292 nm. <sup>b</sup>Buffers used are P = phosphate and C = carbonate.

points were collected for a least-squares linear regression analysis of  $\ln (A_f - A_\infty)$  vs. time, where  $A_\infty$  and  $A_f$  are the final absorbance and the absorbance at any time, respectively. First-order rate constants are given in Table III with the standard deviations for individual runs. Under acidic conditions, the reactions were monitored by following the formation of Br<sub>2</sub> at 390 nm or the formation of Br<sub>3</sub><sup>-</sup> at 266 nm. At 390 nm, both Br<sub>2</sub> and Br<sub>3</sub><sup>-</sup> ( $\epsilon$  = 600 M<sup>-1</sup> cm<sup>-1</sup>) contribute to the absorbance. The formation equilibrium constant for Br<sub>3</sub><sup>-</sup> is 17 M<sup>-1</sup>. Absorbance vs. time data were obtained for more than 4 half-lives with a Durrum stopped-flow spectrometer interfaced to a Hewlett-Packard computer (HP 2100S).<sup>11</sup> First-order rate constants ( $k_{\text{obsd}}$ , s<sup>-1</sup>) were determined from least-squares linear regression analysis of 250 data points. The first-order rate constants in Table IV are given for the average of at least five runs for each set of conditions with the standard deviations for these runs. Experimental rate constants ( $k'_{\text{obsd}}$ ) larger than 80 s<sup>-1</sup> were corrected for mixing effects<sup>12</sup> in accord with eq 7, where  $k_m$  is 1700 s<sup>-1</sup>. The corrected values are given in Table IV.

$$k_{\text{obsd}} = k'_{\text{obsd}} / [1 - (k'_{\text{obsd}} / k_m)] \quad (7)$$

Commercial hypochlorite solutions are prepared from chlorine and NaOH and therefore contain approximately equimolar chloride ion concentrations. For the studies under acidic conditions, the HOCl solution was adjusted initially to pH 5 so that the Cl<sub>2</sub> formation (eq 8) was



negligible (Table II). The forward and reverse rate constants for eq 8

- (6) Wilbur, D. S.; Anderson, K. W. *J. Org. Chem.* 1982, 47, 358-359.  
 (7) Bell, R. P.; Pring, M. J. *Chem. Soc. A* 1966, 1607-1609.  
 (8) Awtrey, A. D.; Connick, R. E. *J. Am. Chem. Soc.* 1951, 73, 1842-1843.  
 (9) Kolthoff, I. M.; Sandall, E. B.; Meehan, E. J.; Brukenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: London, 1969; p 796.  
 (10) Rossotti, F. J. C.; Rossotti, H. J. *Chem. Educ.* 1965, 42, 375-378.

- (11) Willis, B. G.; Bittikofer, J. A.; Pardue, H. L.; Margerum, D. W. *Anal. Chem.* 1970, 42, 1340-1349.  
 (12) Dickson, P. N.; Margerum, D. W. *Anal. Chem.* 1986, 58, 3153-3158.



**Table IV.** Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypochlorous Acid<sup>a</sup>

Buffer Solutions <sup>b</sup>			
[Br <sup>-</sup> ], M	-log [H <sup>+</sup> ]	[buffer] <sub>T</sub> , M	k <sub>obsd</sub> , s <sup>-1</sup>
0.010	5.23	0.05 (A)	24.7 ± 0.4
0.020	5.22	0.05 (A)	46.1 ± 0.5
0.050	5.22	0.05 (A)	115 ± 4 <sup>c</sup>
0.100	5.30	0.05 (A)	245 ± 4 <sup>c</sup>
0.0050	4.78	0.01 (A)	10.83 ± 0.07
0.0050	4.78	0.02 (A)	11.27 ± 0.13
0.0050	4.78	0.05 (A)	12.58 ± 0.05
0.0050	4.78	0.10 (A)	14.65 ± 0.06
0.0050	4.78	0.20 (A)	18.8 ± 0.8
0.0050	2.90	0.01 (C)	16.6 ± 0.2
0.0050	2.87	0.025 (C)	19.44 ± 0.08
0.0050	2.85	0.050 (C)	22.2 ± 0.5
0.0050	2.84	0.100 (C)	27.8 ± 0.4
0.0050	2.83	0.125 (C)	30.0 ± 0.4

Perchloric Acid Solutions		
[Br <sup>-</sup> ], M	10 <sup>3</sup> [H <sup>+</sup> ], M	k <sub>obsd</sub> , s <sup>-1</sup>
0.0020	1.063	6.33 ± 0.05
0.003	1.063	9.75 ± 0.06
0.004	1.063	12.7 ± 0.2
0.005	1.063	16.3 ± 0.3
0.010	1.063	31.7 ± 0.4
0.020	1.063	63.2 ± 0.7
0.005	1.59	19.6 ± 0.2
0.005	2.66	26.4 ± 0.3
0.005	5.84	45.1 ± 0.4
0.005	11.16	81 ± 2 <sup>c</sup>
0.005	21.79	154 ± 2 <sup>c</sup>

<sup>a</sup> [HOCl] = (0.5–6.00) × 10<sup>-4</sup> M, μ = 0.5 M (NaClO<sub>4</sub>), 25.0 °C, λ = 266 or 392 nm. <sup>b</sup> Buffers used are A = acetic acid and C = chloroacetic acid. <sup>c</sup> Rate constants are corrected for mixing.<sup>12</sup>

are 2.8 × 10<sup>4</sup> M<sup>-2</sup> s<sup>-1</sup> and 28.6 s<sup>-1</sup> at μ = 0.5, 25.0 °C.<sup>13</sup> Under all conditions, the calculated rate of formation of Cl<sub>2</sub> was less than the observed rate of formation of Br<sub>2</sub>.

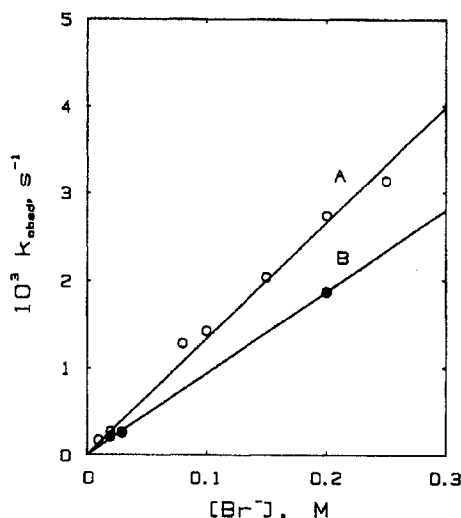
## Results and Discussion

**Reaction of Bromide with Hypochlorite in Base.** Farkas et al.<sup>1</sup> used second-order unequal-concentration conditions, variable ionic strength (0.030–1.049), and a limited pH range (10.8–13.2) to measure the rate of reaction 1. They monitored the reaction by withdrawal of aliquots of the reaction mixture, followed by a dual-titration procedure to distinguish OCl<sup>-</sup> from OBr<sup>-</sup>. The data were fit to the rate expression  $-d[\text{OCl}^-]/dt = k[\text{HOCl}][\text{Br}^-]$ . They extrapolated the experimental data to zero ionic strength to obtain a value of 2.95 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> for *k* at 25 °C, based on a *K*<sub>a</sub> value of 3.2 × 10<sup>-8</sup> for HOCl. In the present work, reaction 1 is studied at constant ionic strength (0.50) under pseudo-first-order conditions with bromide ion in large excess. The bromide concentration is varied from 0.10 to 0.250 M, and the hydroxide ion concentration is varied from 0.0056 to 0.450 M (Table III). Individual reactions give excellent first-order plots, and the *k*<sub>obsd</sub> values are proportional to the Br<sup>-</sup> concentration (Figure 1). The *k*<sub>obsd</sub> values are inversely proportional to OH<sup>-</sup> concentration but have a small intercept (Figure 2). Farkas<sup>1</sup> did not observe a hydroxide-independent term, because of the limitations of the method of observation and the variation in ionic strength. Our experimentally observed rate expression is given in eq 9, where *k*<sub>0</sub> = (0.9 ± 0.1) × 10<sup>-3</sup> M<sup>-1</sup> s<sup>-1</sup> and *k*<sub>1</sub> = (6.64

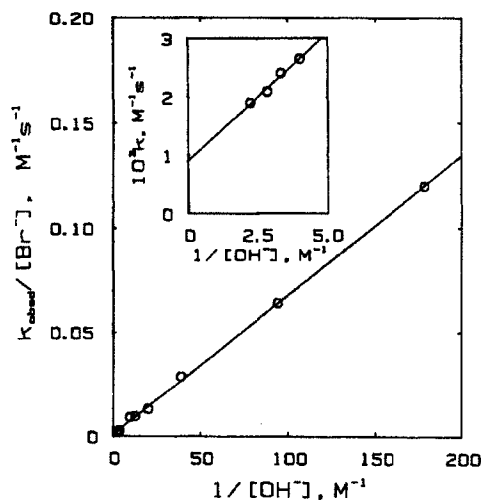
± 0.09) × 10<sup>-4</sup> s<sup>-1</sup> at 25.0 °C. The base-dependent rate constant can be expressed in terms of [H<sup>+</sup>], *k*<sub>H</sub> = *k*<sub>1</sub>/*K*<sub>w</sub> = 3.65 × 10<sup>10</sup> M<sup>-2</sup> s<sup>-1</sup> (p*K*<sub>w</sub> = 13.74 at μ = 0.5, 25.0 °C),<sup>13</sup> or in terms of a

$$-d[\text{OCl}^-]/dt = [k_0 + (k_1/[\text{OH}^-])][\text{Br}^-][\text{OCl}^-] \quad (9)$$

± 0.09) × 10<sup>-4</sup> s<sup>-1</sup> at 25.0 °C. The base-dependent rate constant can be expressed in terms of [H<sup>+</sup>], *k*<sub>H</sub> = *k*<sub>1</sub>/*K*<sub>w</sub> = 3.65 × 10<sup>10</sup> M<sup>-2</sup> s<sup>-1</sup> (p*K*<sub>w</sub> = 13.74 at μ = 0.5, 25.0 °C),<sup>13</sup> or in terms of a



**Figure 1.** Pseudo-first-order rate constants (25.0 °C, μ = 0.50) for the reaction of OCl<sup>-</sup> and Br<sup>-</sup> in base: (A) 0.0493 M NaOH; (B) 0.0972 M NaOH.



**Figure 2.** Inverse hydroxide ion dependence of *k*<sub>obsd</sub>/[Br<sup>-</sup>] for the reaction of OCl<sup>-</sup> + Br<sup>-</sup> in base (25.0 °C, μ = 0.50). The insert shows *k* = *k*<sub>obsd</sub>/[Br<sup>-</sup>] at high hydroxide concentrations, where the intercept is the small hydroxide-independent rate constant, *k*<sub>0</sub> = 0.9 × 10<sup>-3</sup> M<sup>-1</sup> s<sup>-1</sup>.

second-order rate constant of 1.32 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> for the reaction of HOCl (p*K*<sub>a</sub> = 7.44). Thus, HOCl is 1.5 × 10<sup>6</sup> times more reactive than OCl<sup>-</sup> in its reaction with Br<sup>-</sup>.

The rate of reaction 1 is increased by an increase in buffer concentration at constant hydrogen ion concentration, as seen in Table III for hydrogen carbonate and hydrogen phosphate. This behavior is consistent with our previous studies,<sup>2</sup> and the data can be fit to eq 10 and 11, where HA is the acid form of the buffer,

$$k_{\text{obsd}} = (k_0 + k_H[\text{H}^+] + k_{\text{HA}}[\text{HA}])[\text{Br}^-] \quad (10)$$

$$(k_{\text{obsd}} - k_0)/([\text{H}^+][\text{Br}^-]) = k_H + k_{\text{HA}}[\text{buffer}]_T/(K_a + [\text{H}^+]) \quad (11)$$

[buffer]<sub>T</sub> is the total buffer concentration, and *k*<sub>HA</sub> is the general-acid-catalyzed rate constant. Figure 3 shows the general-acid catalysis effect for HCO<sub>3</sub><sup>-</sup>, *k*<sub>HA</sub> = (1.25 ± 0.15) × 10<sup>2</sup> M<sup>-2</sup> s<sup>-1</sup>, and for HPO<sub>4</sub><sup>2-</sup>, *k*<sub>HA</sub> = 8.9 ± 1.3 M<sup>-2</sup> s<sup>-1</sup>.

**Acid-Assisted Reactions of Bromide with Hypochlorous Acid.** Equations 5 and 6 give the stoichiometry in acid, where the formation of Br<sub>3</sub><sup>-</sup> (or Br<sub>2</sub>) is followed by stopped-flow methods. The pseudo-first-order rate constants (Table IV) are directly proportional to the bromide concentration (Figure 4), but are now much larger because HOCl is the dominant species. Despite the

(13) Margerum, D. W.; Gray, E. T.; Huffman, R. P. In *Organometals and Organometalloids, Occurrence and Fate in the Environment*; Brinckman, F. E., Bellama, J. M., Eds.; ACS Symposium Series 82; American Chemical Society: Washington, DC, 1978; pp 278–291.

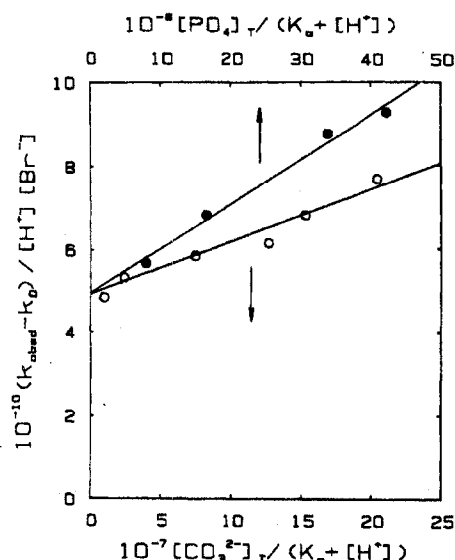


Figure 3. Plot of eq 11 for the general-acid-catalyzed reactions of  $\text{OCl}^- + \text{Br}^-$  by  $\text{HPO}_4^{2-}$  (top) and  $\text{HCO}_3^{2-}$  (bottom).

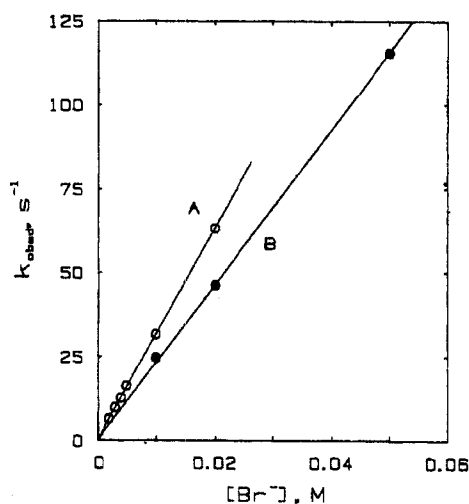


Figure 4. Pseudo-first-order rate constants (25.0 °C,  $\mu = 0.50$ ) for the reaction of  $\text{HOCl}$  and  $\text{Br}^-$ : (A)  $[\text{H}^+] = 1.063 \times 10^{-3} \text{ M}$ ; (B)  $-\log [\text{H}^+] = 5.22$  (0.05 M acetate buffer).

fact that additional acid is not needed to give  $\text{HOCl}$ , the rates again increase with the concentration of general acids (eq 12).

$$\text{rate} = (k' + k'_H[\text{H}^+] + k'_{\text{HA}}[\text{HA}])([\text{Br}^-][\text{HOCl}]) \quad (12)$$

The large increase in the second-order rate constant (for the  $\text{HOCl}$  reaction with  $\text{Br}^-$ ) with increase in  $\text{H}_3\text{O}^+$  concentration is shown in Figure 5. The intercept,  $k' = 1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , is in excellent agreement with the value of  $1.45 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  calculated for this rate constant from the high-pH data. The slope in Figure 5 gives a  $k'_H$  value of  $1.32 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$  for the reaction of  $\text{H}^+ + \text{HOCl} + \text{Br}^-$ .

The rates of reaction between  $\text{HOCl}$  and  $\text{Br}^-$  also increase in the presence of acetic acid and chloroacetic acid (Figure 6). The intercepts differ in this figure because different concentrations of  $\text{H}_3\text{O}^+$  are present in the two cases. The  $k'_{\text{HA}}$  values, obtained from the slopes in Figure 6, are  $(2.09 \pm 0.01) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$  for  $\text{CH}_3\text{COOH}$  and  $(6.1 \pm 0.3) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$  for  $\text{ClCH}_2\text{COOH}$ .

Figure 7 shows the calculated dependence of the second-order rate constant between  $[\text{Br}^-]$  and  $[\text{OCl}^-]_{\text{T}}$  from 1 M  $\text{H}_3\text{O}^+$  to 1 M  $\text{OH}^-$ , when no buffers are present (eq 13). At pH 14 the rate

$$k = k_{\text{obs}}/[\text{Br}^-] = (k_0 + k_H[\text{H}^+] + k'_H K_H[\text{H}^+]^2)/(1 + K_H[\text{H}^+]) \quad (13)$$

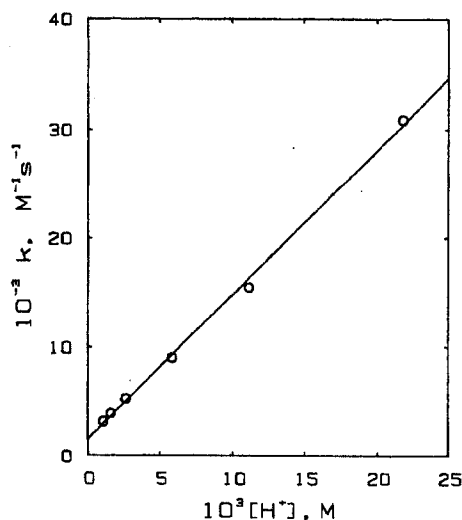


Figure 5. Dependence of the second-order rate constant ( $\text{HOCl} + \text{Br}^-$ ) on  $\text{HClO}_4$  concentration.

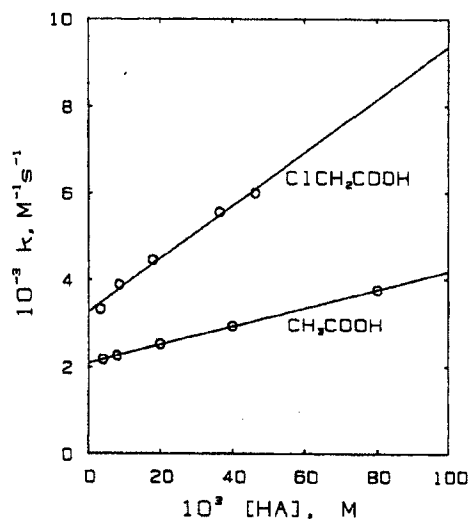


Figure 6. Dependence of the second-order rate constant ( $\text{HOCl} + \text{Br}^-$ ) on the concentration of general acids.

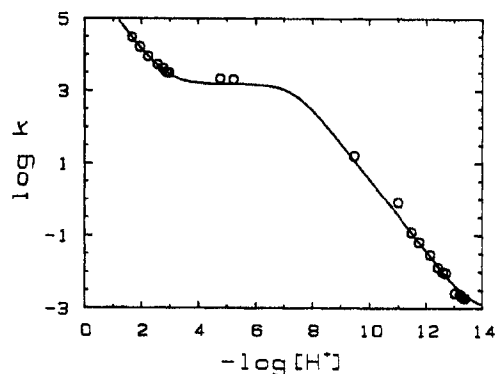


Figure 7. Dependence of the second-order rate constant (in terms of  $[\text{OCl}^-]_{\text{T}}$  and  $[\text{Br}^-]$ ) on the acidity (without buffer catalysis effects).

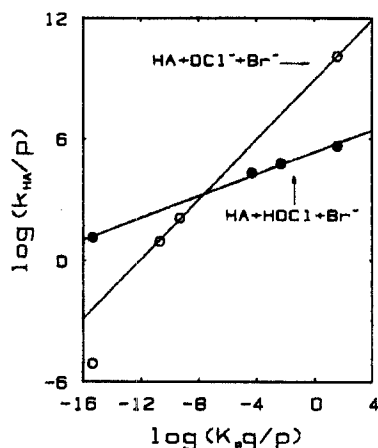
is due mostly to the reaction of  $\text{OCl}^-$  and  $\text{Br}^-$ . From pH 3 to 13 the rate is carried by  $\text{HOCl} + \text{Br}^-$ , but the  $\text{p}K_a$  of  $\text{HOCl}$  (7.44) affects the observed rate constant. Below pH 2 the rate increases due to the reaction of  $\text{H}^+$  with  $\text{HOCl}$  and  $\text{Br}^-$ .

**Brønsted Relationship.** The buffer-catalyzed rates for these reactions increase with the strength of the general acids that are

**Table V.** Third-Order General-Acid-Catalyzed Rate Constants ( $M^{-2} s^{-1}$ ) for the Oxidation of Bromide by Hypochlorite and Hypochlorous Acid<sup>a</sup>

HA	pK <sub>a</sub>	k <sub>OCI<sup>-</sup></sub>	k <sub>HOCl</sub>
H <sub>3</sub> O <sup>+</sup>	-1.72 <sup>b</sup>	$(3.65 \pm 0.05) \times 10^{10}$	$(1.32 \pm 0.03) \times 10^6$
ClCH <sub>2</sub> COOH	2.6 <sup>c</sup>		$(6.11 \pm 0.34) \times 10^4$
CH <sub>3</sub> COOH	4.6 <sup>d</sup>		$(2.09 \pm 0.01) \times 10^4$
HCO <sub>3</sub> <sup>-</sup>	9.8 <sup>e</sup>	$(1.25 \pm 0.15) \times 10^2$	
HPO <sub>4</sub> <sup>2-</sup>	11.3 <sup>f</sup>	$8.9 \pm 1.3$	
H <sub>2</sub> O	15.52 <sup>g</sup>	$(1.6 \pm 0.3) \times 10^{-5}$	27.9 ± 5.5

<sup>a</sup> 25.00 °C,  $\mu = 0.5$  M. <sup>b</sup> Reference 14, p 300. <sup>c</sup> Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5, p 287. <sup>d</sup> Feldman, I.; Koval, L. *Inorg. Chem.* **1963**, *2*, 145–150. <sup>e</sup> MacInnes, D. A.; Belcher, D. J. *J. Am. Chem. Soc.* **1935**, *57*, 1683–1685. <sup>f</sup> Sillen, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, No. 17, 180. <sup>g</sup> Lagerstrom, G. *Acta Chem. Scand.* **1959**, *13*, 722–736. The value is calculated by dividing  $K_w$  by the water molarity, 55.5 M.

**Figure 8.** Brønsted plots for the general-acid-assisted reactions of  $OCl^-$  and  $Br^-$  and of  $HOCl$  and  $Br^-$ .

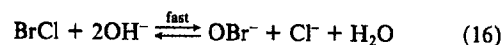
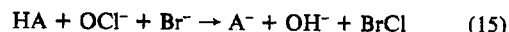
present in the solution. The rate constants (Table V) depend on the Brønsted relationship<sup>14</sup> in eq 14, where  $p$  is the number of

$$k_{HA}/p = G_A(K_A q/p)^\alpha \quad (14)$$

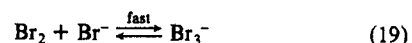
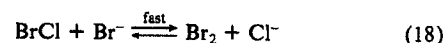
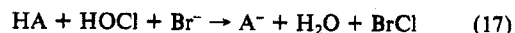
equivalent acidic protons in HA,  $q$  is the number of equivalent basic sites in A,  $K_A$  is the acid dissociation constant of HA,  $G_A$  is a proportionality constant, and  $\alpha$  is the Brønsted coefficient. Figure 8 shows the Brønsted plot for both reaction systems. The slope gives an  $\alpha$  value of 0.75 for the  $HA + OCl^- + Br^-$  reaction, while the  $\alpha$  value for the  $HA + HOCl + Br^-$  reaction is 0.27. The rate constant for the  $H_2O + OCl^- + Br^-$  reaction (the lower left-hand point in Figure 8) falls off the Brønsted correlation. If the immediate reaction products are  $OH^- + OH^- + BrCl$ , the difficulty in generating adjacent hydroxide ions may lower the effectiveness of this path. (A least-squares line through the three points for  $H_2O$ ,  $HPO_4^{2-}$ , and  $HCO_3^-$  gives an  $\alpha$  value greater than unity, which is not possible. Even an  $\alpha$  value of unity would be inconsistent with the experimentally observed general-acid catalysis.) The  $\alpha$  value in the case of other  $HA + OCl^-$  reactions with  $Br^-$  is very close to the value observed in the case of the reaction of hypochlorite with iodide.<sup>2</sup> Although the  $\alpha$  values are similar, the rates are  $10^5$  faster for iodide as compared to bromide. The reactivity of bromide is lower because bromide is a poor nucleophile compared to iodide. The much larger  $\alpha$  value for  $HA + OCl^- + Br^-$  as compared to  $HA + HOCl + Br^-$  reflects the larger degree of proton transfer to  $OCl^-$ , which is a better base than  $HOCl$ . The  $pK_a$  value of  $H_2OCl^+$  has been estimated to be in the region of -3 to -4.<sup>15</sup>

(14) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 198.

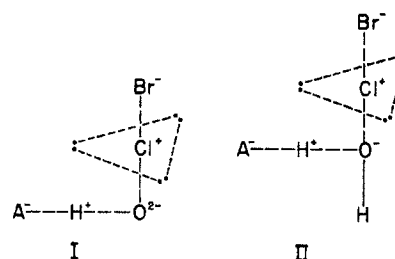
**Proposed Mechanisms.** General-acid-catalyzed kinetics are consistent with the mechanism given in eq 15 and 16 for the reactions in base.



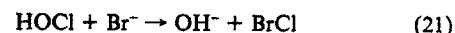
The proposed general-acid-assisted mechanism for the reactions in acid is given by eq 17–19.



In these reactions,  $Cl^+$  is transferred to  $Br^-$  to form  $BrCl$ , a highly reactive intermediate. The similarity of the reactions of  $OCl^-$ ,  $NH_2Cl$ , and  $NHCl_2$  with  $I^-$  to the reactions of  $OCl^-$  and  $HOCl$  with  $Br^-$  strongly suggests a parallel  $Cl^+$ -transfer mechanism.<sup>2</sup> The proposed transition states in structures I and II have

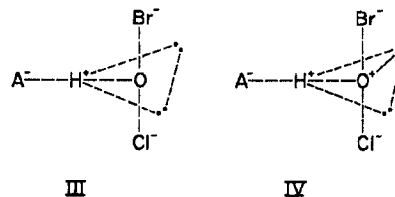


an expanded coordination number for chlorine, which is not at all unusual for this atom. The fact that the reactions in eq 15 and 17 are general-acid catalyzed requires that proton transfer take place as the reactions pass through the transition state. A prior proton equilibration step would remove the dependence on the concentration of HA and result in catalysis only by  $H_3O^+$ . This distinction cannot be made when  $HA = H_3O^+$ , and in this case prior protonation is possible to give the reactions in eq 20 and 21. The third-order rate constant for  $H_3O^+ + OCl^- + Br^-$



equals  $3.65 \times 10^{10} M^{-2} s^{-1}$ . The magnitude of this rate constant requires some degree of prior association between two of the species, even if the third species reacts with this pair at a diffusion-controlled rate. Hence, the bimolecular steps in eq 20 and 21 are suggested and are consistent with the rate constant for reaction 21 ( $1.55 \times 10^3 M^{-1} s^{-1}$ ) that is measured directly in acid. Nevertheless, the  $H_3O^+$  value for the third-order rate constant in eq 15 falls on the Brønsted plot with the other general acids.

An alternate mechanism with transfer of  $HO^+$  or  $H_2O^{2+}$  between  $Cl^-$  and  $Br^-$  is much less likely. It is more difficult to expand the coordination of oxygen as compared to chlorine, and the transition states in structures III and IV would be high-energy



states. This path would be expected to have much smaller rate constants as is the case for carbon analogues.<sup>2</sup> Furthermore, it is not clear why protons should necessarily assist oxygen atom

(15) Arotzki, J.; Symons, M. C. R. *Q. Rev. Chem. Soc.* **1962**, *16*, 282–297.

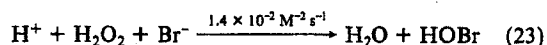
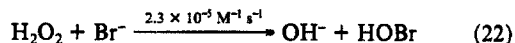
**Table VI.** Third-order Rate Constants for the Oxidation of Halides by Hypochlorite and by Hypohalous Acids

reactants	$k$ , $M^{-2} s^{-1}$	ref
$H^+ + OCl^- + Br^-$	$3.65 \times 10^{10}$	a
$H^+ + OCl^- + I^-$	$4.4 \times 10^{15}$	b
$H^+ + HOCl + Cl^-$	$2.8 \times 10^4$	c
$H^+ + HOCl + Br^-$	$1.3 \times 10^6$	a
$H^+ + HOBr + Br^-$	$1.6 \times 10^{10}$	d
$H^+ + HOI + I^-$	$4.4 \times 10^{12}$	d

<sup>a</sup>This work. <sup>b</sup>Reference 2. <sup>c</sup>Reference 13. <sup>d</sup>Reference 5.

transfer reactions (i.e. why  $HO^+$  and  $H_2O^{2+}$  should react much more rapidly than the oxygen atom).

Reactions are known in which a halide reacts as a nucleophile at an oxygen atom, for example the bromide reactions with hydrogen peroxide:<sup>16</sup>



In these cases  $OH^-$  and  $H_2O$  are leaving groups, in a manner

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similar to structures I and II where  $OH^+$  replaces  $Cl^+$ . On the other hand, the above  $H_2O_2$  rate constants are factors of  $1.5 \times 10^8$  and  $1.1 \times 10^8$  slower than the corresponding reactions of  $HOCl$ . This is consistent with a less favorable nucleophilic attack by bromide ion at oxygen as compared to chlorine.

In the  $Cl^+$ -transfer mechanism, protonation of the oxygen atom greatly assists the rate because  $OH^-$  and  $H_2O$  are suitable leaving groups. Since the  $O^{2-}$  ion is not an appropriate leaving group, water must donate a proton if the  $k_0$  path ( $H_2O + OCl^- + Br^-$ ) also occurs by  $Cl^+$  transfer.

Table VI summarizes the third-order  $H_2O^+$ -assisted rate constants for the reactions of hypochlorite and hypohalous acids with halide ions. The relative reactivity for  $H^+ + OCl^-$  with halides is  $I^- \gg Br^-$  and for  $H^+ + HOCl$  with halides is  $Br^- \gg Cl^-$ . The increase in reactivity with  $I^- \gg Br^- \gg Cl^-$  reflects the relative nucleophilicity of the halide ions. The rate constants for  $H^+ + HOX + Br^-$  show that  $HOBr$  is more reactive than  $HOCl$ , even though the  $HOCl$  reaction is more favorable thermodynamically. The relative reactivity of  $HOCl$ ,  $HOBr$ , and  $HOI$  parallels the ability to more easily expand the coordination of  $X$  and transfer  $X^+$  to the halide ion.

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Registry No.  $Br^-$ , 24959-67-9;  $OCl^-$ , 14380-61-1;  $HOCl$ , 7790-92-3.

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## Removal of Iron from Transferrin by Pyrophosphate and Tripodal Phosphonate Ligands

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The kinetics of iron removal from transferrin in 0.1 M HEPES buffer at pH 7.4 and 25 °C have been studied by visible spectroscopy. Pseudo-first-order rate constants have been determined as a function of the ligand concentration for the ligands pyrophosphate, nitrilotris(methylenephosphonic acid), *N*-(phosphonomethyl)iminodiacetic acid, *N,N*-bis(phosphonomethyl)glycine, and nitrilotriacetic acid. The general equation that describes this ligand dependence is  $k_{\text{obs}} = k[L]/(1 + k'[L] + k''[L])$ . The results are discussed in terms of two parallel pathways for iron removal, one that is first order in ligand and another that shows saturation kinetics. Iron removal by the phosphonic acids proceeds predominately through the saturation pathway, while iron removal by the structurally related ligand nitrilotriacetic acid proceeds exclusively through the first-order pathway. Iron removal by pyrophosphate is relatively rapid through both pathways, so that the saturation process predominates at low ligand concentration and the first-order pathway predominates at higher ligand concentrations.

### Introduction

Serum transferrin is the primary mammalian iron transport protein. The protein has been extensively studied, and several recent reviews of transferrin chemistry are available.<sup>1-3</sup> Transferrin consists of two major lobes, designated N-terminal and C-terminal, with a single high-affinity iron-binding site associated with each lobe. These sites are well separated, and although they are very similar, they are not identical.

Serum transferrin belongs to a small class of proteins that includes ovotransferrin and lactoferrin. The distinguishing characteristic of these proteins is the requirement of a synergistic anion for effective metal binding. Under physiological conditions the anion is (bi)carbonate, which binds simultaneously to the iron and to cationic side groups on the protein to form an  $Fe-HCO_3^-Tf$  ternary complex. Under carbonate-free conditions, reasonably stable ternary complexes can be formed with a variety of other anions.<sup>4</sup>

At sites of iron utilization, ferric transferrin binds to specific cell membrane receptors and releases its iron, although the process by which iron is removed from the very stable transferrin complex is still not clearly understood.<sup>5</sup> Iron removal from transferrin could

also be important in chelation therapy for chronic iron overload. Certain genetic disorders such as  $\beta$ -thalassemia require frequent transfusions of whole blood. Since the body is unable to excrete the iron contained in this blood, it accumulates to lethal levels in organs such as the heart.<sup>5</sup> As a serum protein, transferrin is readily accessible to therapeutic chelating agents, but the rate of iron removal by desferrioxamine B, the current drug of choice, is quite slow.<sup>5,6</sup> Thus there is considerable interest in ligands that can remove iron from transferrin more quickly.

Rates of iron removal by several classes of ligands, including phosphonic acids,<sup>7</sup> catecholates,<sup>8,9</sup> hydroxamates,<sup>10,11</sup> and pyrophosphate,<sup>12,13</sup> have recently been reported. In all cases a hyperbolic dependence of the rate of iron removal on the concentration of ligand was reported. In enzyme kinetics this type of

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# APPENDIX

## O



US006669904B1

(12) **United States Patent**  
**Yang et al.**

(10) **Patent No.:** **US 6,669,904 B1**  
(45) **Date of Patent:** **Dec. 30, 2003**

(54) **STABILIZED BROMINE SOLUTIONS,  
METHOD OF MAKING AND USES  
THEREOF FOR BIOFOULING CONTROL**

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**162/70**

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**423/462, 500; 210/754; 252/186.36, 187.2;**  
**162/70**

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(57) **ABSTRACT**

Stabilized bromine solutions are prepared by combining a  
bromine source and a stabilizer to form a mixture, and then  
adding an oxidizer to the mixture.

**20 Claims, No Drawings**

1

# STABILIZED BROMINE SOLUTIONS, METHOD OF MAKING AND USES THEREOF FOR BIOFOULING CONTROL

## REFERENCE TO RELATED PATENT

This application is a continuation-in-part of U.S. Ser. No. 09/283,122, filed on Mar. 31, 1999 now U.S. Pat. No. 6,270,722.

## FIELD OF THE INVENTION

This invention relates generally to water treatment and, more particularly, to stabilized bromine solutions, method of making and uses thereof for biofouling control.

## BACKGROUND OF THE INVENTION

Sodium hypochlorite has been widely used in a variety of industrial and recreational water systems to control biofouling. However, sodium hypochlorite is unstable and must be provided in a stabilized form. There are several methods known in the art for stabilizing hypochlorite (See, e.g., U.S. Pat. Nos. 3,328,294 and 3,767,586).

Bromine is preferred over chlorine for use in water treatment because of its lower volatility and better performance at high pH and amine environments. However, like sodium hypochlorite, sodium hypobromite is unstable in typical storage conditions and must therefore also be provided in a stabilized form. U.S. Pat. Nos. 5,683,654 and 5,795,487, as well as the references disclosed therein, teach various methods for stabilizing sodium hypobromite. The '654 and '487 patents disclose batch methods which utilize sodium hypochlorite and sodium bromide as starting materials, followed by the addition of a stabilizer. WO 97/20909 similarly discloses a process which includes a hypobromite formation step followed by a bromine stabilization step. However, a disadvantage associated with this technique is that unstabilized hypobromite is formed in a separate step at a high concentration and pH. It is known that unstabilized hypobromite degrades quickly under such conditions to form bromate, a non-biocidal compound that is very toxic and a suspected carcinogen.

In addition, WO 97/43392 discloses a process that first forms stabilized chlorine compounds and then converts them to stabilized bromine compounds. However, this type of process is limiting because only hypochlorite-releasing compounds can be used as the oxidizing source.

Therefore, because the demand for stabilized bromine solutions is expected to increase in the future due to its advantages over chlorine, there is a need for other cost-effective methods of making stabilized bromine which can use a wider range of oxidants.

Accordingly, it would be desirable to provide a method of making a stabilized bromine solution which can be carried out as a batch or continuous process right at the site of the commercial application. It would also be desirable to develop a method of making a stabilized bromine solution which is flexible and allows a variety of oxidizers to be utilized.

## SUMMARY OF THE INVENTION

The stabilized bromine solutions of the present invention are prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

The inventive method is economically appealing because it can be carried out as a batch or continuous process at the

2

commercial application site, thereby eliminating the need to store and transport the stabilized bromine solutions. The method of preparation is also flexible and allows for the utilization of a variety of oxidizers.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method of making stabilized bromine solutions. In accordance with this invention, a bromine source and a stabilizer are combined to form a mixture, and then an oxidizer is added to the mixture.

The bromine sources which may be used in the practice of the present invention include hydrobromic acid, and alkali or alkaline earth metal bromides, such as sodium bromide, potassium bromide and lithium bromide.

The stabilizers which may be employed in this invention have the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected from the group consisting of  $R^2CO$ ,  $R^2SO_2$ ,  $R^2CF_2$ ,  $R^2CHF$ , H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic group. Suitable stabilizers include saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid and its alkali or alkaline earth metal salts, organic sulfamates and melamine. Sulfamic acid and its alkali or alkaline earth metal salts are the most preferred stabilizers.

Optionally, other water treatment chemicals, such as tracing compounds, surfactants, corrosion inhibitors and scale inhibitors, can be added to the bromine/stabilizer mixture.

The oxidizers which may be used include chlorine gas, hypochlorous acid, hypochlorite salt, chlorite, chlorate, elemental bromine, bromine chloride, hydrogen peroxide, persulfate, permanganate and peracetic acid. Chlorine gas, hypochlorous acid and hypochlorite salt are the most preferred oxidizers. It is believed that other peroxy compounds can also be used in accordance with this invention.

The stabilized bromine solutions which are prepared in accordance with this invention can be prepared at the site of the commercial application. This eliminates the need to store and transport the stabilized bromine solutions and thus the need for adding caustic to adjust the pH and extend the shelf life of the solutions. The present invention can be carried out as either a batch or continuous process.

It is preferred that the molar ratio between the bromine source and the stabilizer be in the range of about 0.1 to 10. The molar ratio between the bromine source and the oxidizer should preferably be in the range of about 0.2 to 5.

The stabilized bromine solutions which are prepared in accordance with this invention may be used in a wide variety of commercial applications. These applications include, but are not limited to, the use of the stabilized bromine solution: (1) as the bleaching agent in a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent; (2) as the oxidizing agent in a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached; (3) as the oxidizing and biocidal agent in a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling; (4) as the oxidizing and biocidal agent in a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface; (5) in a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters; (6) in

a method for controlling biofouling in an aqueous system; (7) in a method for controlling biofouling in pulp and paper manufacturing process water and process chemicals; and (8) in a method for controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream.

In another embodiment, the invention is a method of preventing biofouling on the surfaces of equipment in contact with an industrial water system. The method comprises adding an effective biofouling controlling amount of a stabilized bromine solution to the water system, wherein the solution is prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

The types of industrial water systems in which the stabilized bromine solution may be used to prevent biofouling include, but are not limited to, cooling water systems, sweetwater systems, gas scrubber systems, air washer systems, evaporative condensers, pasteurizers, produce sanitizer streams, fire protection water systems and heat exchanger tubes.

It is preferred that the amount of stabilized bromine solution which is added to the industrial water system be in the range of about 0.1 ppm to about 2000 ppm and preferably in the range of about 0.5 ppm to about 500 ppm, based on available chlorine concentration. The stabilized bromine solution can be added to the water system by any conventional method, i.e., by slug, intermittently or continuously.

### EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

#### Example 1

This example demonstrates the impact of caustic addition. It also illustrates that caustic addition is not needed if the inventive stabilized bromine solutions are prepared and used at the site of the commercial application.

Three stabilized bromine formulations were prepared with the only difference being their caustic contents. The formulations underwent an accelerated thermal degradation test at 135° F. and the product actives were determined by potassium-thiosulfate titration at various times. The half lives of the products were calculated from first order decay curves. As shown below in Table 1, the product half lives indicate that the lower the caustic addition, the shorter the shelf life.

TABLE 1

Raw material	Formulation (moles)		
	A	B	C
Sodium hydroxide	0.176	0.628	5.808
Sulfamic acid	0.126	0.126	0.126
Water	0.488	0.488	0.488
Sodium hypochlorite	0.09	0.09	0.09
Sodium bromide	0.09	0.09	0.09
Product half life (days)	1.8	41.3	41.3

#### Example 2

A laboratory experiment was conducted at room temperature (70° F.) by:

1. Preparing a mixture (solution A) of sodium bromide and sodium sulfamate to contain 33.3% wt of sodium bromide and 17.4% of sodium sulfamate in water;
2. Adding 0.76 ml of 10.9% wt (as available chlorine) chlorine bleach to 1000 ml of synthetic cooling water containing 225 ppm (as  $\text{CaCO}_3$ ) hardness and 125 ppm (as  $\text{CaCO}_3$ ) total alkalinity (solution B); and
3. Adding 0.241 ml of solution A to solution B to form the final solution.

One milliliter of the final solution was taken at different time points and diluted 100 times in deionized water. The halogen residual concentrations in the diluted solution were determined using Hach's DPD method 80 on a DR-2000 spectrophotometer. Three types of DPD measurements were taken: (1) free halogen residual using free chlorine reagent and read at 20 seconds after the reagent was added to the test solution, (2) total halogen residual using total chlorine reagent, and (3) 3-minute halogen residual using free chlorine reagent and read at 3 minutes after the reagent was added. As discovered by the inventors, the difference between the total halogen residual and 3-minute halogen residual is the concentration of N-chlorosulfamate.

While determining the halogen residual in the solution, another one milliliter of the final solution was taken and added to a flask containing 100 ml of the synthetic cooling water with  $2.4 \times 10^6$  CFU/ml of cooling water mixed culture bacteria. After five minutes of mixing, an aliquot of sample was taken from the flask and neutralized with sodium bisulfite. The surviving bacterial population was enumerated on 3M's aerobic count Petrifilm® media after appropriate dilution. The test results are summarized below in Table 2.

TABLE 2

Time (minutes)	Halogen residual concentration (ppm as avail. $\text{Cl}_2$ )			
	Free halogen	3-minute free	Total halogen	log reduction of bacterial count
10	0.56	0.56	0.92	>6.3
30	0.48	0.60	0.91	>6.3
66	0.57	0.66	0.93	>6.3
135	0.63	0.70	0.93	>6.3
180	0.63	0.76	0.95	>6.3

The results show the effective biocidal performance of the prepared solution. In addition, the solution was found to be stable and there was no reduction of total halogen residual during the test period while the concentration of N-chlorosulfamate decreased with an increase in the N-bromosulfamate concentration.

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications and equivalents included within its spirit and scope, as defined by the appended claims.

What is claimed is:

1. A method of making a stabilized bromine solution comprising the steps of:

- a. combining a bromine source and a stabilizer to form a mixture; and
- b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.



5

2. The method of claim 1 wherein the bromine source is selected from the group consisting of hydrobromic acid, alkali earth metal bromides and alkaline earth metal bromides.

3. The method of claim 1 wherein the stabilizer has the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected from the group consisting of  $R^2CO$ ,  $R^2SO_2$ ,  $R^2CF_2$ ,  $R^2CHF$ , H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic group.

4. The method of claim 1 wherein the stabilizer is selected from the group consisting of saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monochloramine, diethanolamine, organic sulfonamides, biuret, sulfamic acid and its alkali or alkaline earth metal salts, organic sulfamates and melamine.

5. The method of claim 1 wherein the stabilizer is selected from the group consisting of sulfamic acid and its alkali or alkaline earth metal salts.

6. The method of claim 1 wherein the molar ratio between the bromine source and the stabilizer is in the range of about 0.1 to 10.

7. The method of claim 1 wherein the molar ratio between the bromine source and the oxidizer is in the range of about 0.2 to 5.

8. A stabilized bromine solution produced by the method of claim 1.

9. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprising using as the bleaching agent the stabilized bromine solution of claim 8.

10. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprising using as the oxidizing agent the stabilized bromine solution of claim 8.

11. In a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

12. In a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

13. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field

6

waters, the improvement comprising adding to the produced oil field waters an effective biofouling controlling amount of the stabilized bromine solution of claim 8.

14. A method of controlling biofouling in an aqueous system which comprises adding to the aqueous system an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

15. A method of controlling biofouling in pulp and paper manufacturing process water and process chemicals which comprises adding to the process water an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

16. A method of controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream which comprises adding to the aqueous stream an effective, microbial growth controlling amount of the stabilized bromine solution of claim 8.

17. A method of preventing biofouling on the surfaces of equipment in contact with an industrial water system which comprises adding to the water system an effective biofouling controlling amount of a stabilized bromine solution, said solution having been prepared by the steps of:

a. combining a bromine source and a stabilizer to form a mixture; and

b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.

18. The method of claim 17 wherein the industrial water system is selected from the group consisting of a cooling water system, sweetwater system, gas scrubber system, air washer system evaporative condenser, pasteurizer, produce sanitizer stream, fire protection water system and heat exchanger tube.

19. The method of claim 17 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.1 to about 2000 ppm as available chlorine.

20. The method of claim 17 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.5 to about 500 ppm as available chlorine.

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